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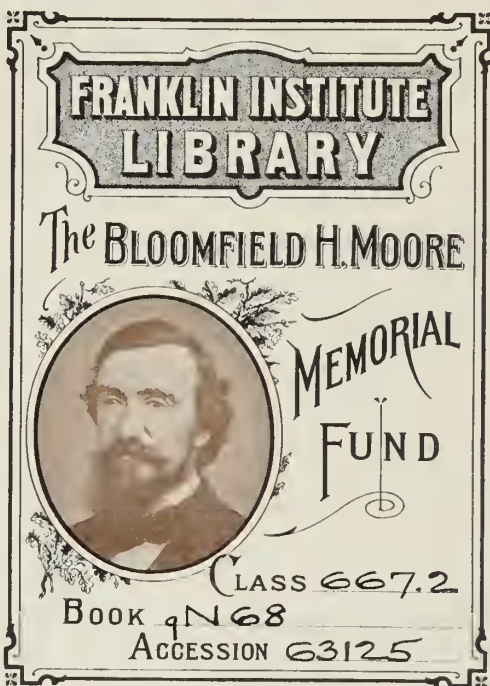
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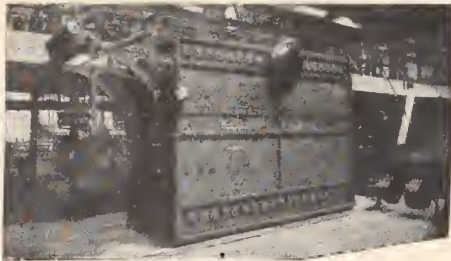
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ANILINE BLACK

AND ITS APPLICATIONS
IN DYEING AND PRINTING.



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ANILINE BLACK

AND ITS APPLICATIONS
IN DYEING AND PRINTING

BY

E. NOELTING, — AND — A. LEHNE,

*Director of the Mulhouse Chemical
School.*

*Privy Councillor, President of
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Translated by ARTHUR MORRIS

Editor of the "Dyer & Calico Printer."

With numerous Illustrations, and Specimens of Dyed and
Printed Fabrics.



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Translator's Preface.

ANILINE Black had hardly commenced to assume great technical importance before the practice of this branch of the textile colouring industries, in France at least, was greatly hampered by a long series of patents taken out by a Paris chemist, W. J. S. Grawitz. The first of these appeared in 1874 and, patent quickly succeeding patent, Grawitz actively and aggressively claimed to monopolise the industry. The easy ways of the British patent office made it a simple matter to claim the same monopoly in England, but it must be noted that not one of the specifications of Grawitz satisfied the inspection of the German patent authorities. In the French law courts the mere possession of a patent was a strong point in favour of Grawitz, and in the course of many lawsuits he was generally able to defend his position. As the situation quickly became intolerable to the French textile colouring industry, it was to be expected that a champion of the common weal would be found, and a very powerful one arose in the person of Dr. E. Noelting, director of the School of Chemistry of Mulhouse. With infinite patience and labour he compiled a complete history of aniline black, and by a careful analysis of the Grawitz patents, specification by specification, he sought to prove that anything in them that was good was not new, and that anything that was new was not good.

The work appeared in French in 1889, and Messrs. Wm. J. Matheson and Co., of New York, recognising its importance, brought out an English translation the same year. Dr. A. Lehne in 1892 collaborated with the original author, and a much enlarged work appeared in German. This was republished, again with additions, in 1904, and the second German edition is the basis of the present book. The French edition of 1908, however, is not a simple translation of the original. M. O. Piequet gave his assistance not only as translator, but as collaborator, and the text was completely revised by Dr. Noelting, who added much new matter, bringing the work completely up to date.

Grawitz, therefore, whatever be the merits of his highly aggressive claims, has been the cause of the production of a very com-

plete monograph on a technical subject of the highest importance. His patents have expired, and the examination of them occupies little space in the present volume. The pages are better utilised by a full account of all recent work on the constitution of aniline black, the application of the black to the dyeing of half-wool and to the latest processes of producing an ungreenable black. The names of the collaborators, Noelting, Lehne and Piequet, are a guarantee of the value of the volume, and will insure it as favourable a reception in its English dress as in the original German and French.

Very considerable additions have been made to this present edition, with the object of bringing it up to date. In this task the translator has had the valued assistance of several technical chemists of world-wide reputation. Dr. C. Noelting has heartily co-operated once more, Dr. Fussgaenger has revised and partially re-written some of the most important chapters, the chemists of the B.A.S.F., and the Hoechst Farbwerke have carefully amended all that portion relating to their specialities, and Messrs. Mather and Platt have provided entirely new diagrams of their very latest machines, and have also thoroughly revised the descriptions of them.

The metric system has been retained throughout the work. The conversion of several hundred recipes from grammes and litres to ounces and gallons would give opportunity for mistake, whereas one of the chief beauties of the metric system is that the relation between the litre and the gramme allows a recipe to be converted at sight into "parts by weight." One litre of water is 1000 grammes, 1 c.c. is 1 gramme; the specific gravity of any other liquid of course expresses the weight in grammes of one litre, if the figure is brought to three places of decimals and the decimal point is then discarded.

March, 1909.

ARTHUR MORRIS.

CHAPTER I.—The History of Aniline Black.

EARLY RESEARCHES.

Just as the discovery of aniline red (Magenta) may be attributed to the observations of Natanson and Hofmann, so it may be admitted that the principle of the formation of aniline black was foreshadowed in the old-time researches of Runge, Fritzsche and A. W. Hofmann.

Runge (*M.S.* 1860, p. 533), in 1834, noted the following facts:—

When chloride of copper is added to nitrate of “kyanol” (as he called aniline) heated to about boiling point, a dark green colouration is produced which quickly turns to black.

A drop of hydrochloride of aniline, with a little bichromate of potash added, heated to boiling point, gives a spot of deep black in which a reddish colouration may be noted. Hydrochloride of aniline printed on a fabric previously treated with bichromate gives, after twelve hours, a green fast to washing.

Fritzsche (*J.P.C.*, 1840, p. 454), in 1840, working with aniline obtained by the dry distillation of indigo, noted that when chromic acid is added to a solution of aniline salt there is a precipitate which is sometimes dark green, and at other times blue black. This precipitate is always produced, even in very dilute solutions of aniline salt, and therefore chromic acid may be regarded as an excellent reagent for the detection of aniline. Even when the precipitate is formed in acid solution it leaves after calcination a large proportion of oxide of chromium.

Fritzsche (*J.P.C.*, 1843, p. 293) endeavoured, without success, to determine the constitution of the new bodies thus obtained. He was unable to reproduce them in an invariable form. They varied according to the quantity of chromic acid used and the acidity of the solutions, and products looking identically alike gave very varied results on analysis, the contents in carbon oscillating between 33.93 and 63.66 per cent., and the oxide of chromium between 31 and 2.12 per cent.

Fritzsche (*J.P.C.*, 1843, p. 202) also noted that on pouring a solution of chlorate of potash acidulated with hydrochloric acid into a mixture of equal volumes of alcohol and aniline salt solution, a flocculent precipitate of a beautiful indigo blue is slowly formed, and settles at the bottom of the beaker. The slower the reaction the more successful is the result. When concentrated solutions are employed a pasty mass is obtained.

The precipitate, filtered and washed with alcohol, loses its blue

tint in proportion as the acidity diminishes, and turns greenish. After drying, a dark green powder remains, of greatly lessened volume. It contains 16 per cent. of chlorine, and appears to correspond with the formula:—



The mother liquor treated with chlorate of potash and hydrochloric acid gives chloranile.

It is evident that the combined action of chlorate of potash, hydrochloric acid, and an oxidisable body, such as alcohol, produces chlorous acid or other compounds of chlorine containing still less oxygen. Doubtless this led Hofmann (*L.A.*, xliii., p. 66) to study the action of chlorous acid on hydrochloride of aniline. He thus obtained Fritzsche's blue substance very easily and instantaneously.

Beissenhirtz (*L.A.*, lxxvii. p. 367) remarked that the action of concentrated sulphuric acid and a few drops of bichromate of potash solution on aniline or its salts produced a pure blue colouration which disappeared after some time.

Crace Calvert, Clift and Lowe (Lectures, 1861), at the same time as Wilm, obtained Fritzsche's green-blue colour by the action of chlorate of potash on hydrochloride of aniline, and had the happy idea of producing the reaction on the fibre.

Wilm mixed chloride of iron with nitrate of aniline, and at the end of a short time obtained a violet colouration, and also a blue precipitate. The same reaction is produced when the chloride of iron is replaced by bichromate of potash.

J. Persoz had noted the production of the green-blue colour when a mixture of hydrochloride of aniline and chloride of iron is heated gently.

Emile Kopp (*M.S.*, 1861, p. 75) repeated Fritzsche's experiments and studied the action of various oxidants on aniline.

C. Lauth observed the production of aniline blue by the action of peroxide of hydrogen. He added gradually 2 parts of di-oxide of barium to a solution of one part of aniline in 10 parts of hydrochloric acid, made up to 100 parts by the addition of water. At the end of some hours he obtained an abundant precipitate of aniline blue, giving the same reaction as that got with chlorate of potash. This reaction is not produced by the peroxide of hydrogen and the sulphuric acid; the presence of hydrochloric acid is necessary, as this, under the influence of the peroxide, gives up chlorine or even compounds of chlorine and oxygen. Aniline and peroxide of hydrogen in solution in acetic acid give no trace of the black.

The blue colour, turned green by acids, was named emeraldine by Crace Calvert, Clift and Lowe.

When emeraldine is developed on the fibre by means of nitrate of aniline and chlorate of potash in the presence of a ferric salt or other oxidant, or when the colour produced on the fibre is oxidised by means of a dilute solution of bichromate of potash or

chloride of lime, a black is obtained. We shall return to this reaction in treating of the production of aniline black on the fibre.

Perkin, who discovered Mauveine, in 1856, in preparing this colour, obtained substances which are certainly analogous to the oxidation products of emeraldine. When cold solutions of equal molecular weights of sulphate of aniline and bichromate of potash are mixed, a black pulverulent precipitate is produced after 10 of 12 hours. This is filtered, washed and dried, then treated with light coal-tar oils to free it from tarry matters, continuing the treatment as long as the oil takes a brown colour, and finally washed with alcohol to separate out a violet colouring matter.

The residue is aniline black in powder, insoluble in ordinary solvents. This powder contains a considerable quantity of oxide of chromium, and it has not yet been precisely determined whether this is chemically combined in the black, or is in intimate mixture with it. The black thus obtained as a by-product in the manufacture of Mauveine, is not emeraldine, as sometimes asserted, but is a highly-oxidised product, which is hardly greened by the action of sulphurous acid.

It is evident that Perkin's sulphate of aniline contained a slight excess of acid, as according to Charles Girard, it produced bichromate of aniline when used in absolutely neutral solutions. This bichromate of aniline is precipitated from concentrated solutions, but remains in solution when they are diluted. Perkin's Violet soon became a commercial product, and many processes for its production were patented or described. In all these processes, including those of Perkin himself, the yield of violet colour is poor, and the most abundant product of the reaction is the black.

Bolley, Beale and Kirkham, C. Lauth, and P. Depouilly, used a solution of chloride of lime; Greville Williams equivalent solutions of sulphate of aniline and permanganate of potash. Kay heated 50 parts of aniline, 40 of sulphuric acid at 66° B., 1,400 of water, and 200 of black oxide of manganese to the boiling point.

Price, by adding one equivalent of peroxide of lead to a boiling solution of one equivalent of aniline in two equivalents of sulphuric acid, obtained a violet colour (Mauveine), and by using two equivalents of peroxide of lead he obtained a red colour (Safranine). In either case the black was formed as a by-product.

Dale and Caro boiled for three hours one equivalent of a salt of aniline (acetate, hydrochloride, sulphate, or nitrate), with 6 equivalents of chloride of copper.

The black precipitate, after extraction of the violet colour which it contained, was as early as 1862 sold to the calico printers for use as an albumen colour. Up to that time the aniline blue and the aniline black in powder were merely laboratory products, obtained in the preparation of the violet. In 1865 and onwards patents were taken out for processes for a special production of the black.

Bobœuf (*B.F.*, 68,079, 1865) obtained the black by adding acid to mixed solutions of hydrochloride of aniline and bichromate of potash or, preferably, by adding a solution of one part aniline in 2 or 3 parts of hydrochloric acid at 20° or 22° B., to a solution of bichromate of potash. Fritzsche, it will be remembered, used an aniline salt and chromic acid. According to the salt of aniline employed the precipitate is black or of a varying blue tint.

Alland (*B.F.*, 68,230, 1865) boiled a solution of 20 grammes of aniline in about 100 grammes of hydrochloric acid and poured gradually into this 5 to 6 grammes of caustic potash (!) and 10 grammes of bichromate of potash. This liquid poured into a solution of chloride of lime and of soda at 5° B. gives at once a black precipitate, which may be used as pigment colour in textile printing.

Alfred Paraf (*B.S.M.*, August, 1865) prepared chlorate of aniline by the action of hydrofluosilicate of aniline on chlorate of potash. This solution does not produce a black by simple boiling, but the addition of a few drops of hydrochloric acid instantly gives a black precipitate. This black contains no trace of a metallic compound. It has the great advantage of not turning green on exposure to the air.

According to a note which appeared in the *Moniteur Scientifique*, 1864, p. 443, the insoluble residue of the preparation of Perkin's Mauve with bichromate was used in textile printing as an albumen colour for grey and black.

Dullo (*W.J.*, 1866, p. 599) obtained aniline black in powder by treating hydrochloride of aniline with bichromate of potash or with a mixture of chloride of iron and chlorate of potash. He also produced it by oxidising an acid solution of an aniline salt by means of permanganate of potash. To develop the black on the cotton fibre, Dullo mordanted with iron, worked the goods in a very dilute solution of aniline and then oxidised. He does not state by what means the oxidation was carried out.

In 1871 (*W.J.*, 1871, p. 775) the firm of Heyl Bros. and Co., of Charlottenburg, were selling an aniline black for albumen printing. Armand Muller, of Zurich, in the same year describes the preparation of a black analogous to that of Heyl Bros., possibly even identical. He had then used it for two years in cotton printing with success. He dissolved 20 grammes of chlorate of potash, 30 grammes of sulphate of copper, 16 grammes of sal-ammoniac, and 40 grammes of hydrochloride of aniline in 500 c.c. of water, heated the mixture in the water bath to about 60° C., then lifted it out of the water bath. In two or three minutes the mixture swells up, sometimes even runs over, and gives off vapour with the odour of chloropierine, probably due to the formation of chloroquinone or chloranile. When the mass is not entirely black at the end of a few hours, it is heated anew to 60° C. It is left in the open air for a day or two, washed on the filter

until the mineral salts are eliminated, and made into a paste containing about 50 per cent. of water. This paste is dried in a vacuum, and takes the form of an amorphous powder of a very deep black. According to Muller, its formula is $C_{12}H_{14}N_2O_{11}$, but Nietzki has shown that this is incorrect. It will be necessary to return to this point.

Rheineck (*D.P.J.*, cciii., p. 485), at Elberfeld, in 1872, obtained an aniline black by dissolving equal parts of aniline (containing toluidine), hydrochloric acid and chlorate of potash in sufficient water, adding a little chloride of copper and allowing the mixture to rest at the ordinary temperature. He turned it into a porcelain dish, allowed it to dry in the air, moistened it anew, repeating the drying and moistening until he obtained a black powder with greenish reflex. All the aniline is transformed into black, and an excess of chlorate is recovered. After careful washing the powder leaves no residue on calcination, and the yield is 120.5 per cent. of the aniline used, which, it must be remembered, contained toluidine.

The black thus obtained is the hydrochloride of a base which is dark violet in a free state. Carbonate of soda or carbonate of ammonia takes from it 8.9 per cent. of hydrochloric acid. The base is very energetic, and is capable of replacing aniline in its salts. A fent impregnated with the violet base is dyed green by the action of hydrochloride of aniline even in the presence of an excess of aniline.

The aniline black, while still green before treatment with alkalis, when acted upon by concentrated sulphuric acid, gives off hydrochloric acid fumes, just as any hydrochloride will. The sulphuric acid gives a violet solution, and on addition of water a greenish black precipitate falls down, which is simply the sulphate of the base.

Rheineck repeated his experiments with pure aniline and then obtained a yield of black of 114.8 per cent. Both with the pure and the impure aniline a very slight quantity of soluble organic matter is produced, and therefore the reaction may be looked upon as very sharp. According to an analysis, the proportion of nitrogen eliminated in the form of ammonia is one-eighth to one-ninth of that contained in the aniline; other analyses make it still less.

Rheineck gave to the base of the black the name of Nigraniline.

Glanzmann (*B.S.M.*, 1874) sent to the Mulhouse Society five patterns of black obtained in different ways but all equally fast. All the five were fast to acids, alkalis and light, and did not green even after stripping to a light grey. Their fastness was comparable with that of lamp-black, and the prints had not the disagreeable yellowish tone of this colour. As a rule, the blacks could be used without the addition of blue.

The first of these blacks was made by boiling a solution of aniline salt, and adding to it successively and gradually a solution of sulphate of copper, then bichromate of potash, keeping the

whole at the boil for three hours. After washing and drying the black powder obtained contained 20 per cent. of organic black and 80 per cent. of oxides of copper and chromium.

In the second experiment the salt of copper was left out. A liquid containing aniline, bichromate of potash, and water was heated to 60° C., dilute hydrochloric acid was poured in gradually, and the mixture was boiled for two hours, or until the mass, at first thick, became more fluid. After washing and drying, the black obtained was found to contain 60 per cent. of organic black and 40 per cent. of oxide of chromium.

It is not necessary to use salts of aniline; it is equally permissible to oxidise aniline directly with bichromate. In this case also, the black obtained contains a heavy proportion of oxide of chromium, which appears to be combined with the organic matter and to give to the black its good properties of fastness. Analysis shows that the proportions of oxide of chromium are fairly constant. To separate this completely out the black must be destroyed; after treatment with *aqua regia* a swollen mass remains which burns without residue.

In the remaining three experiments the black was obtained by direct oxidation with bichromate solutions of varied strength. The three blacks obtained, when washed and dried, contained 58, 57 and 53 per cent., and 42, 43 and 47 per cent. of oxide of chromium respectively. The yield of black increased with the quantity of bichromate employed, whereas the composition of the product was little modified and the content in oxide of chrome was approximately the same.

THE GRAWITZ PATENTS.

Samuel Grawitz, on September 30th, 1874, took out in France his first patent for the production of aniline black on fibres of all natures and for the manufacture of the colour as a dry powder or in the form of a paste.

The Grawitz patents have all expired. They were the cause in France of a large number of legal suits, the issue of which, as a rule, was in favour of the plaintiff. The necessity of discussing *la chose jugée* has passed. Persoz, C. Girard and Noelting among others have debated the matter, and shown luminously that the numerous patents taken out by Grawitz had no practical value and, moreover, absolutely lacked novelty. Nevertheless, from the historical point of view, and also to allow our readers to form a personal opinion, by comparing the processes described in the foregoing pages with the Grawitz patents, it is necessary to reproduce the specifications. It must be noted that in Germany, where there is a preliminary examination as to novelty before a patent is granted, none of the applications of M. Grawitz was accepted.

B.F. 105,130, September 30, 1874. For the production of aniline black on fibre of any nature, and in paste or as dry powder, suitable for employment as colours of all kinds.

My processes are based on the following reaction:—

When aniline oil is made to re-act on any per-salt of iron or copper, a salt of iron or copper anile is formed, which is very easily oxidised by the action of a chlorate or a soluble chromate, producing a very beautiful and very fast black.

To produce a black in paste or as a dry powder suitable for use for textile printing with albumen or any other fixing agent, or for making colours, varnishes and inks, I operate as follows:—

Into a solution of a per-salt of iron or copper I pour aniline oil and add a solution of a chlorate or soluble chromate.

The best proportions are those which correspond as regards the aniline, the iron or copper salt, and the chlorate or soluble chromate to their chemical equivalents.

I leave the reaction to operate in the cold for some hours or energeise it by heat. A black precipitate is formed, which I collect and wash on a filter.

This black precipitate in paste has great covering powers, and is eminently suitable for printing fabrics of all kinds, the colour being fixed with albumen or any other analogous substance.

In this manner aniline black may be associated with all other colours in printing.

To produce aniline black on the fibre itself, which may be either silk, wool, linen or cotton, I proceed in two distinct manners.

1. I print, by means of suitable thickenings, a mixture of the three reagents indicated, aniline, a per-salt of copper or iron, and a chlorate or soluble chromate. The colour develops rapidly on exposure. It appears in all its beauty after washing and scouring.

2. I print on the fabric a salt of metal anile and then pass it through a bath of a chlorate or soluble chromate. I may also print on a mixture of aniline with a chlorate or soluble chromate and pass through a bath of a per-salt of iron or copper.

The principal advantages of my process, as apart from the yield, which is enormous, are as follow:—

1. The economy. This is evident.
2. The absence of all free acid which would attack the metal with which the pieces come into contact.
3. The possible absence of all trace of copper which might be deposited on the doctors and steel rollers.

I claim, therefore, as my exclusive property for fifteen years the right to make aniline black, whether prepared in advance or developed on the fibre by one of the two following processes in whatever manner it may be used.

Mutual reaction of aniline oil with a per-salt of iron or copper or a soluble chromate.

The following recipes are extremely economical:

Sulphate of copper, bichromate of potash, aniline oil.

Sulphate of peroxide of iron, bichromate of potash, aniline oil.

In place of aniline oil a neutral aniline salt may be employed.

This constitutes an important improvement on the processes in use in which an acid is added; but this method increases the cost and does not improve the products. I claim it nevertheless.

This is the ensemble of the processes and applications that I claim as my property for fifteen years by virtue of the present patent.

Certificate of Addition to above patent, dated October 3, 1874.

When it is desired to produce on fibres themselves (whatever their nature, silk, wool, linen or cotton), my aniline black, which results from the concomitant action on aniline or its salts of bichromate of potash (and more generally of a soluble chromate) and of per-salts of iron and copper, this is done with the usual starch thickenings, and therefore the colour develops very badly and very slowly.

The development is much more rapid with the salts of aniline than with aniline oil, and still more so with the salts and an excess of any acid.

I therefore modify my process in the following manner:—

As regards the black in paste and powder, there is no necessity to make a change. Nevertheless production of the black is more rapid and much easier with the salts of aniline, and still more with the salts and an excess of acid. I claim, therefore, the preparation thus extended.

In order to develop the black on the fibre, I print with the aid of thickenings:—

1. A salt of aniline, a per-salt of iron or copper, and bichromate of potash, or a soluble chromate, and expose to the air. Or

2. I print the preceding mixture with excess of acid. Or

3. I print a salt of aniline, and a per-salt of iron or copper, and I pass through a bath of bichromate of potash or a soluble chromate with excess of a free acid.

I also claim, by the present certificate the right to apply to the dyeing of fabrics or yarn of silk, wool, linen or cotton, my aniline black, resulting from the *concomitant action on aniline or its salts of the per-salts of iron or copper and of soluble chromates or bichromates.*

To dye, I pass the yarn or fabric through a bath prepared with a mixture of salts of aniline and of per-salts of iron or copper.

I then pass through a bath containing soluble chromates or bichromates and excess of acid.

In all these operations the blacks produced vary in tone according to the acid, combined whether with the aniline, the iron or copper, or free in the chromate bath, from blue-black to maroon, passing by violet-black and black.

B.F. 105,554, November 3, 1874.

The object of the present patent is to reserve to myself the exclusive right of dyeing with aniline black or shades approaching black, such as maroon, blue-black, or violet-black, on all textile materials of whatsoever nature they may be, in the raw state, yarn or fabrics.

The colour is developed by the concomitant action on aniline oil, or on its salts of the following reagents:—

1. Chromates or bichromates or soluble chlorates.
2. Salts of iron, of copper, of manganese, of nickel, of cobalt, or others in their highest degree of oxidation. The proto-salts may also be employed as they pass into the state of salts of the sesquioxide in the process itself, but the shades are less beautiful.

The nature of the black I produce is very probably a black of metal anile. One molecule of hydrogen in the aniline is replaced by a metallic molecule, and this complex base is oxidised by the soluble bichromates or chromates, or by the chlorates.

To put the operation into action I may operate in two different manners:—

I may steep the textile fibres in aniline oil, drain, then pass in a solution of a metallic salt, which immediately forms a precipitate fixed on the fibre, containing aniline and metal. Then I pass through a bath of a soluble bichromate, acid or not.

This process is difficult to carry out.

The following one is better.

A bath is made containing salts of aniline and copper, the fibre is mordanted in this bath and oxidised by soluble chromates or bichromates or even chlorates. It is best to have the double metallic and aniline salts well combined, for example, when iron is used, the ferrocyanides and ferricyanides of aniline.

The following proportions give good results. I reserve to myself the right to vary them.

For cotton, and for hemp and linen thread:—

1 litre of water.

125 grammes hydrochloride of aniline.

85 grammes bichloride of copper.

50 grammes nitrate of sesquioxide of iron.

Allow the material to become saturated in the bath, then pass into a bichromate solution, and after thorough draining, wringing out and rinse as required.

The bichromate bath gives the best results when it is cold and dilute. For cotton it may be very slightly acidified with organic or mineral acids in the proportions necessary to saturate the alkali of the bichromate, or even to hold in solution all the oxide of chromium arising from its reduction. This is the best process, but is not invariably advisable.

For wool, silk, hair, and feathers it is preferable to begin by dyeing the silk, wool, etc., either in nitric acid or in chromic acid to a yellow, then operate as above except that acid salts of aniline and metal may be used and the chromate bath acidified more strongly, without fear of tendering the fibres.

According to the nature of the acids entering into the composition of the different salts, shades from maroon to blue passing by violet and black are thus obtained.

When very black shades are desired, attention must be paid

to the purity of the aniline. This is the ensemble of the processes and applications that I claim as my property for fifteen years by virtue of the present patent.

The order of the passages through the bath may be inverted.

B.F. 105,555, November 3, 1874.

For the production of a series of colours from aniline and salts of other alcaloids such as toluidine, rosaniline more or less substituted, naphthylamine, etc.

The method which I intend to reserve to myself for the production of a series of colours in dyeing or printing is based on this fact:—Substitution in aniline or other organic alcaloids for one or several molecules of hydrogen, of one or several molecules of a metal, whatever it may be, then oxidation of the complex base that results by chromates or bichromates, or even soluble chlorates in neutral or even acid liquors, by chlorides and hypochlorites by steaming or by aeration, oxidising at above the ordinary temperature.

Instead of forming the complex base I may bring the metallic alcaloid elements together in the state of salts so as to obtain the elements of a double salt, fixed by dyeing or printing, and then oxidised by the means already stated.

The metallic molecule taking the place of a molecule of hydrogen, gives very great stability to the subsequent products of oxidation, on account of the stability of metallic oxides and the affinity of metals for oxygen.

My complex bases may be compared to ammonide of copper. They will be anilide of copper, rosanilide of copper, naphthylamide of copper or of iron, etc.

My complex salts may be compared to double ammoniacal salts. I reserve to myself all the alcaloids and all the metals as regards this special reaction.

When iron is employed a convenient method is to form the ferrocyanide or ferricyanide of the base.

As these salts or their bases will require further oxidation, it is evident that metallic salts at their highest degree of oxidation should be employed to begin with.

This is the ensemble of the processes and applications that I reserve to myself for use in dyeing and printing.

B.F. 121,581, May 18, 1878.

The invention consists in replacing the salts of iron or copper which figure in the primitive recipe given by John Lightfoot for the production of aniline black in presence of chloric acid, by chromic acids or its compounds.

Certificate of Addition to B.F. 105,130, April 29, 1875.

In the present demand for a certificate of addition to my patent of September 30, 1874, I again describe my method for the production of black or shades approaching black by the concomitant

re-action on aniline oil or its salts, of certain metallic salts and of chromates or bichromates.

The salts capable of giving a black are the salts of the following metals:—

Iron, copper, manganese, cerium, aluminium, chromium, nickel, cobalt, tungsten, vanadium, lead, etc., in general, all the metals capable of presenting two degrees of oxidation and susceptible of transformation from one to another. For example, iron, of which the salts of the protoxide are changed into the sesquioxide by the fixation of oxygen, and of which the salts of the sesquioxide are transformed into those of the protoxide by reduction.

To apply this reaction I proceed in two distinct manners:

1. Production of a black, in paste or in dry powder, insoluble in all the reagents suitable for printing textiles or paper, and for making colours, varnishes and inks of all kinds.
2. Production of black on the textile fibre itself.

1. *Production of the Black in Paste or in Dry Powder.*

This is the best manner of working:

I pour sufficient oil of aniline to produce a precipitate into a solution of a per-salt of iron, for instance. Then I pour into the semi-fluid mass which is produced, a solution of bichromate of potash. A precipitate is formed which I wash on the filter or by decantation, at first with pure water, then with alkaline water, in order to destroy the greenish reflex.

The total quantity of acid used should be sufficient to neutralize the bichromate of potash and the oxide of chromium resulting from the reduction of the chromic acid.

The reaction is energised by elevation of the temperature.

2. *Production of the Black on the Fibre by Printing.*

I may operate in the three following ways:—

1. I print with the aid of a suitable thickening, starch, gum-tragacanth or other, a mixture of : 1st, a salt of aniline; 2nd, a metallic salt of the metals above indicated; 3rd, bichromate or soluble chromate. I develop the colour by exposure.

2. I print a mixture of a salt of aniline with an organic acid, and an easily decomposable metallic chromate, and steam.

3. I print a mixture of a salt of aniline, and a metallic salt of the metals indicated above, and pass into a dilute neutral solution, or better, an acid solution, of a soluble chromate or bichromate.

The proportion of the aniline in the mixture varies from 5 to 10 per cent.

The best relative proportions of aniline, of the metallic salt, and of chromate or bichromate is that of their chemical equivalents.

In order to dye textile materials black with aniline, a salt of iron, for example, is employed.

I form a bath A containing for 100 litres:—

Hydrochloric acid of 10 to 20° B.	...	8 litres.
Aniline oil	4 „
Liquid perchloride of iron at 45° B.	...	4 „

made up with water.

I also form a second bath, containing:—

Water	1,000 litres.
Bichromate of potash	8 kilos.

I first mordant the textile materials in bath A, drain and squeeze out with care the excess of liquid which I collect, then I put the materials thus mordanted to digest for five or six hours in the second bath B.

The bath B is sufficient to develop the colour on 200 kilos of cotton, for instance.

I then wash the cotton lifted from bath B in cold water, then in lukewarm water, wring out the water, and recommence the same series of operations, that is to say:—

1st. Mordanting in the bath A.

2nd. Digestion in the bath B; and so on in repetition until a sufficiently dark shade is obtained.

The operation is finished when the material, perfectly washed on leaving the chromate bath with cold and then with warm water, shows a brown reflex.

At this point, after thorough washing with boiling water, on passing the cotton through a boiling soap bath containing about 10 grammes per litre, the shade is turned to a bluish black. Carbonate of soda gives a violet shade.

For piece goods the mordanting may be done by padding, and the colour developed by passing the pieces at full width through a vat with rollers or other suitable apparatus.

The rapidity of the development of the colour is accelerated by the *greater concentration of the liquors, and especially by increasing their degree of acidity.*

In dyeing cotton care should be taken not to use anything that may tender the fibre.

The bath of chromate may be replaced by a bath of chlorate, but this is dearer, and the shades not so good; I, however, claim it.

I dye in this manner cotton, linen, hemp, wool, silk, feathers, skins, wood, and in general all materials capable of being damped.

To sum up, I claim the production of black by the concurrent action on aniline oil or its salts of certain metallic salts, and a solution of soluble chromates or bichromates. I also claim the right to apply these reactions, not only with pure aniline, which gives the black, but also with commercial anilines which give shades approaching to black, with toluidine, which gives a brown, with naphthylamine which gives a puce, and alcaloids derived from aniline by substitution, such, for instance, as ethylaniline, methyl-aniline diphenylamine, etc.

This is the ensemble of reactions, products, and applications which I claim by the present certificate of addition.

Certificate of Addition to B.F. 105,554, Aug. 24, 1876.

The object of the present certificate of addition is to recapitulate the chemical reactions which I have patented for the application of aniline to the production of black, or of shades approaching to black; also the processes which I have reserved to myself already, or which I now reserve to myself for use in dyeing textile materials.

By my principal patent of September 30, 1874, perfected on November 3 of the same year, and by the certificates of addition thereto attached I have intended to patent and claim three things:

1. A series of chemical reactions giving, with aniline, black or shades approaching black.
2. A series of processes in order to use these reactions.
3. The application of this ensemble of processes and reactions to the dyeing of textile materials of all kinds, and the claim to the exclusive right of dyeing with aniline, black or shades approaching to black, on materials of animal origin, a result absolutely new and patentable in itself, independent of any process.

The ensemble of chemical reactions, of which I have patented the application to the production of black, the result of the concomitant action on aniline oil or its salts, of certain metallic salts and soluble chromates or bichromates or even chlorates, *without exposure to air*.

I have indicated and patented three principal methods for applying these reactions.

The first consists in the formation of a complex base containing at the same time aniline and a metal, a complex base, which is obtained by precipitating certain metallic salts with aniline oil. These complex bases redissolve in acids.

The second method is the formation of a bath containing a double salt of aniline and a metal. For example, equal equivalents of perchloride of iron and hydrochloride of aniline are used together in the bath.

The third consists in the formation of a bath containing the elements of an aniline salt, combined with a metal, that is to say, the aniline salt of a metallic acid.

This last-mentioned method includes the formation by double decomposition in the baths of ferro and ferricyanides of aniline, of chromates and bichromates, of manganates and permanganates, of tungstates, vanadates and bivanadates of aniline. These complex bases, these double salts of aniline and of metal, these aniline salts of a metallic acid, have the property of allowing the aniline to oxidise progressively with the greatest facility, producing black, or shades approaching black when the oxidation has not had sufficient time.

In applying this ensemble of reactions and processes to the dyeing of textile materials, the operations may be done continuously

or at different times, or in two or three baths, or in a single bath.

In the three bath process the method is as follows:—

The complex bases of which I have spoken are precipitated on the material to be dyed, by passing the materials in any order through aniline, then through a metallic salt, draining carefully between the two baths. The black is then developed by passing the material through a bath of chromates, bichromates, or even soluble chlorates.

For working with two baths there are two distinct ways:—

Allow the materials to become saturated in a bath containing either the elements of a double salt of aniline and a metal; or 2, the elements of an aniline salt of a metallic acid. The materials dyed in this bath take a green, becoming darker and darker, in the cold, and better still with heat. These are true dyeings, for they can be rinsed with impunity. The aniline is then peroxidized and the black developed by passing the materials to be dyed through a bath of chromate, bichromate, or even a soluble chlorate.

To dye in a single bath, there are also two ways:—

Prepare the bath with the metallic elements and aniline alone, and let the material soak in this and take a dark green, then add to the same bath the peroxidant, a chlorate, or a soluble chromate or bichromate.

Or the bath may be made up with all the elements necessary to produce the black in such a state of concentration that they will not be precipitated immediately, but will commence to re-act promptly on the introduction of the material to be dyed, either at the ordinary temperature, which is better when chromates and bichromates are employed, or at a higher temperature, which is better when chlorates are used.

This last manner of operating, by adding at once to the dye-bath all its constituent elements, effects an enormous improvement, especially in dyeing piece goods.

The aniline salts of metallic acids which give the most remarkable results are those in which the metallic acid is chromic acid.

In a bath containing, by double decomposition, the elements of chromate of aniline without excess of chromic acid, the materials are only dyed a dark green, becoming violet blue by passage through an alkali exactly as with the chloride or nitrate of the sesquioxide of iron. When peroxidised by a passage through a soluble bichromate or chromate, this green gives the black. The black is got at once by putting into the bath a sufficient quantity of bichromate or chromate. When a chlorate is used, the quantity of acid in the bath should suffice to saturate the base combined with the chloric acid.

When chlorates and bichromates are employed, not only the base combined with the chromic acid should be saturated, but also the oxide of chromium arising from the reduction of the chromic acid.

The metals, the salts of which give one or another of the

re-actions indicated, are those metals with two degrees of oxidation, easily convertible from one to the other by oxidation or reduction, and especially the following, of which the energy is very great: Iron, copper, manganese, cerium, chromium, nickel, cobalt, tungsten and vanadium.

I reserve to myself the use of all these mineral or organic acids, whether combined with metals or with aniline, or even free in the dye-baths to enter into the preceding re-actions. The shades obtained vary with the nature of these acids.

The processes I have indicated may be combined among themselves, an infinity of proportions may be employed for the dye-bath, but the black will none the less result by means of the re-actions which I have patented, and reserve to myself the application whatever way they may be put into work.

I give two examples of dyeing 100 kilos. cotton. I take—

Water	800 litres.
Bichloride of copper	250 grammes.
Aniline oil	6 kilos.
Hydrochloric acid	24 kilos.
Bichromate of potash	9	„ 600 gr.

I enter the materials at the room temperature, and work them frequently in the bath to begin with, then more slowly. The dyeing is completed in one hour or even less. The black has a bronze reflex which is removed by boiling with soap. The copper may be omitted.

Second example:—

Water	100 litres.
Aniline oil	6 kilos.
Hydrochloric acid at 19° B.	12 „
Chlorate of potash	8 „
Perchloride of iron at 50° B.	8 „

I enter cold or lukewarm and gradually raise the temperature. Wash and soap. Piece goods may be worked in the padding machine or on the winch or in any other suitable apparatus.

Chlorates give poorer blacks than chromates. For certain shades, chromates and chlorates may be combined. When chromates are in the bath it is difficult to use with heating; it is better to work at the ordinary temperature.

I must remark in conclusion, that chromate blacks differ radically from the blacks of Lightfoot in the elements entering into their production, and my chlorate blacks in the method of development, as they do not require exposure. I am the first to have found and applied the discovery that these green or black precipitates which are formed in the baths can be fixed on textile fabrics in the same bath. With suitable proportions the baths remain limpid; all the precipitate is absorbed by the fibre. My chromate blacks are evidently the same that M. Perkin produced together with his violet obtained with chromates, and of which he did not

recognise the importance in 1859—four years before Lightfoot's patent—blacks which have never since been successfully fixed on the fibre.

This is the ensemble of the reactions, processes and applications which are my property, by virtue of my different patents and certificates of addition.

It is unnecessary to add that the weight of aniline in proportion to the textile material may be regulated according to the intensity of the black it is desired to obtain. I have indicated the proportions of the elements of the black preferable for medium shades. When the proportion of aniline is very small, it is better to use less water and increase the proportion of the peroxidising body.

B.F. 115,160, October 21, 1876.

For the Production in Dyeing and Printing of an Inalterable Aniline Black.

The object of the present patent is:—

1. To specify the chemical nature of aniline black in a perfect inalterable state.
2. To determine the conditions of its production.
3. To reserve to myself the exclusive right either to produce it direct or to transform imperfect into perfect blacks.

The blacks in the perfect state present the double specific character that they are not turned green by gaseous or liquid sulphurous acid, and that they do not dissolve in cold sulphuric acid of 66° B., which merely holds them in suspension so that they are precipitated on the addition of water, as a black powder.

The imperfect blacks, the only kind obtained by Lightfoot's process, are turned green by sulphurous acid, and dissolve in sulphuric acid, and are deposited on the addition of water, as a green powder.

All my blacks so far are developed without exposure to air, by the action of chromic acid in solution, or by acid chlorates.

The production of a perfect black requires that the chromic acid should exercise its action at above 80° C., and that the chlorates should exercise their action on steaming.

It is a delicate operation to employ heat when chromic acid is present. It is better to operate as follows:—

Dye cold or lukewarm with 160 to 180 parts of acid bichromate for 100 parts of aniline. The black thus obtained is imperfect. To change the imperfect into perfect black, treat the textile materials, after rinsing, with the following re-agents:—

- | | | | | | | |
|----|-----------------------|-----|-----|-----|-----|------------|
| 1. | Copperas | ... | ... | ... | ... | 20 kilos. |
| | Bichromate | ... | ... | ... | ... | 6 „ |
| | Sulphuric acid 66° B. | .. | | | | 16 „ |
| | Water | ... | ... | ... | ... | 60 „ |
| 2. | Bichromate | ... | ... | ... | ... | 3 kilos. |
| | Water | ... | ... | ... | ... | 10 litres. |
| | Sulphuric acid 66 B. | ... | .. | ... | ... | 2½ „ |

Either 5 litres of re-agent 1, or 2 litres of re-agent 2, is used in 800 litres of water. Heat to above 80° C., and work about three-quarters of an hour, adding a little of the re-agent if necessary.

The chlorates which exert an action of the same kind on steaming are the chlorates of aniline and aluminium. The black always greens a little with chlorates.

Nitrous acid, sulpho-nitric acid and acid oxidizing agents in general have the same action.

The same re-agents transform into perfect blacks the imperfect blacks, which are the only ones given by Lightfoot's process for printing.

The black in the perfect state may have three reflexes, maroon, black, or blue-black.

By abridgment the process gives inalterable greys.

These bodies, perfect black and the inalterable grey, being definite chemical compounds, which I have first produced on fabrics, I reserve to myself their application in dyeing and printing whatever means of producing them may be discovered later.

This is the ensemble of the reactions, processes and applications which I claim in my present patent.

Certificate of Addition of March 22, 1877, to B.F., 105,554.

I noted in my last certificate of addition to my patent of November 3rd, 1874, that it was a delicate operation to use heat when dyeing with chromic acid and chromate of aniline.

To guard against all accidents, the dyeing should be done as follows:—The bath being made up with a salt of aniline and bichromate of potash acidified by an acid in the proportions indicated, conduct the operation entirely in the cold for from one-half to three-quarters of an hour. The temperature may then be raised gradually even to the boiling point, if desired, and kept at about the boil for about half-an-hour.

The heating may be done over the fire or with steam.

The blacks obtained in this manner, as well as those got by the processes already described, in the patents I have taken out, that is to say, mordanting in baths containing a salt of aniline and a per-salt of iron, for example, then oxidation in acid chromate by successive dips in the cold; or by mordanting with the aniline salt of a metallic acid, for example in acid chromate of aniline, then fixing by a passage through a hot bath of per-salt of iron; the blacks, I say, formed in these three ways, or by mixed processes arising from their combination, are insoluble in sulphuric acid, and do not green in the air, nor even under the action of sulphurous acid.

By diminishing the proportion of aniline per kilo. of textile material, quite a series of grey shades more or less deep may also be obtained by the same processes.

Example of a grey on 10 kilos of cotton:—

Water	200 litres
Aniline	250 cc.
Hydrochloric acid, 22° B.	250 cc.
Bichromate of potash	550 grammes.
Sulphuric acid, 66° B.	250 cc.

The presence of metallic salts other than salts of chromium in the dye-bath allows the shades of grey to be varied even more readily than those of the blacks.

These non-greening blacks, these non-greening greys, I am the first to produce and patent as new bodies independent of any process for their production.

The maroon bronze black obtained by dyeing in the cold with chromic acid is very cheap and suitable for many articles.

Blacks may also be fixed by dyeing in the cold, then in a lukewarm bath containing chlorate of potash, a salt of aniline and a ferric salt, for instance, then passing at the boil or near that point through a weak bath of chromic acid, containing also sulphuric acid to hold the oxide of chromium in solution.

Non-reducing acids at about 100 deg. C., also turn the bronze blacks obtained by dyeing in the cold with chromic acid into fast black.

This is the ensemble of processes, products and applications which I intend to reserve to myself by the present certificate of addition.

LATER RESEARCHES.

Coquillion (*C.R.* lxxxi., p. 408) showed in 1875 that aniline black is produced when the current from two Bunsen cells is passed for twenty to twenty-four hours through a concentrated solution of sulphate of aniline. The positive pole, of platinum or carbon, is then covered with a thick black mass, which is washed with alcohol and ether and then gives an amorphous black powder with greenish reflex. This black is coloured green by the action of concentrated sulphuric acid, and is transformed by alkalis into a beautiful velvety black. Hydrogen in a nascent state has no action on it. Nitrate of aniline forms an analogous mass on the platinum electrode, and this also changes to a velvety black under the action of alkalis, and is decomposed by sulphuric acid, giving a maroon. With hydro-chloride of aniline no good result is obtained. The acetate and tartrates give different products.

In a later article (*B.S.C.p.*, xxv., p. 46) Coquillion clearly demonstrated that the black obtained with the nitrate or acetate of aniline, on treatment with sulphuric acid, gives a different black to that obtained with the arseniate, phosphate, hydrochloride, or sulphate of aniline. The black got with the arseniate or phosphate dissolves to a violet red solution in sulphuric acid, and gives a flocculent green precipitate on the addition of water to

this. The black obtained with the hydro-chloride or sulphate of aniline has similar properties, but it is much more rapidly produced by the electric current. The flocculent precipitate, when treated with potash or ammonia, rapidly turns black again. If the electrodes are of carbon, they must be very carefully cleaned.

This proves that the black can be produced by the action of oxygen without the intervention of a metal, thus contradicting the theories previously accepted.

Goppelsroeder's experiments on the electrolytic production of aniline black preceded Coquillion's, although his results were published after these. The two chemists arrived at the same conclusions on the common ground of their researches, but Goppelsroeder did not limit his experiments to aniline; he extended them to a large number of other aromatic bases.

The passage of the electric current through a solution of hydro-chloride or sulphate of aniline produces, to begin with, a greenish efflorescence at the positive electrode. This gradually turns violet, then blue violet, and finally a beautiful deep black, like the blue black of indigo. If the direction of the current is reversed when the precipitate is violet, it loses colour and the colour appears at the electrode that was formerly negative.

The indigo blue precipitate produced at the positive pole is a mixture of various colours, in which aniline black dominates. After washing out the foreign bodies with boiling water and then with alcohol, a beautiful velvety black powder is obtained, insoluble in ordinary solvents and turned a deep green by the action of acids. Fuming sulphuric acid transforms the electrolytic black into a sulphur compound insoluble in water and soluble in alkalis. These alkaline salts in aqueous solution are turned into leuco bases under the action of alkaline reducing agents, such as glucose and hydrosulphite, and regain their oxygen in the air. This suggested to Goppelsroeder the idea of setting an aniline black vat after the manner of the indigo vat, but the process has never come into practice because of the lack of depth in the dyeings obtained in this way.

On analysis of the black as first produced, Goppelsroeder found that its formula was $C_{24}H_{20}N_4HCl$. The black after-treated with an alkali, that is to say, the free base, has a simpler formula, C_6H_5N . This agrees exactly with the results obtained by Nietzki and Kayser, which we shall have occasion to examine later on. Goppelsroeder deduced from his hydro-chloride formula that the rational formula of the base is $C_{24}H_{20}N_4$.

Prud'homme in 1877, as a sequel to Goppelsroeder's work, obtained the sulphur compound of emeraldine by oxidising aniline in solution in concentrated sulphuric acid.

Richard Meyer (*Ber.* ix., p. 141) in the same year prepared aniline black by the action of permanganate of potash on a strongly acid solution of sulphate of aniline. Solutions of the hydro-chloride acid give the same result, but sulphuric acid

is preferable, as the formation of chlorine compounds is thus avoided. By mixing concentrated solutions he obtained a dark olive green precipitate which quickly turned black; this is the sulphate of the black which alkalis turn into a blue black. This is insoluble in ordinary solvents, but it dissolves to a beautiful blue black solution on concentrated sulphuric acid, and is reprecipitated on the addition of water. Meyer does not say whether or not his black is identical with that of Coquillion and Goppels-roeder.

C. Brandt, in 1869, among other bodies analagous to aniline, tried alphanaphthylamine, and this, treated with the same oxidants as aniline, gave a violet brown which has since found some interesting applications.

Prud'homme (*B.S.M.*, 1890, p. 320) made a series of experiments in 1879, on aniline and its various homologues. He did not obtain an ungreenable black with pure aniline without subsequent oxidation. With pure *a-m*-xylidine 1:3:4 he got a brown olive, acids and bisulphite of sodium turned this yellower. Para-toluidine gave a brown, still yellower than the xylidine brown, but less affected by acids. Orthotoluidine gives a black which is not so blue as that produced by pure aniline, but nevertheless is a fine shade and is less affected by acids. A mixture of equal parts of *o* and *p* toluidine should give an excellent black, ungreenable without the necessity of super-oxidation, but it is brownish and not so fine a black as that obtained with pure aniline.

On a bottom of manganese bistre, aniline gives a beautiful fast black. In order to try how the homologues of aniline and of the aminophenols behaved under the same conditions Rettig (*B.S.M.*, 1886, p. 174) dyed a variety of these bases over a bottom of manganese bistre, using a bath containing 4 grammes of the base in the state of normal sulphate and 0.4 gramme of sulphuric acid per litre. The bistre dyed cloth was entered into the cold bath and the temperature was raised in three quarters of an hour to 55 deg. C. After dyeing, the cloth was rinsed and soaped. In this way he tried the three toluidines, the five xylidines, the two cumidines, and aminotetramethylbenzene, with the following results:—

O—toluidine	1 : 2	Blue-black, fast.
M—toluidine	1 : 3	Plum colour.
P—toluidine	1 : 4	Cutch brown, not fast.
O—xylidine	1 : 2 : 3	Reddish mode, fast.
O—xylidine	1 : 2 : 4	Mode, not fast.
M—xylidine	1 : 3 : 4	Reddish brown, not fast.
M—xylidine	1 : 3 : 5	Tobacco brown, fast.
P—xylidine	1 : 4 : 2	Grey, fine and fast.
Cumidine	1 : 3 : 5 : 2	Chamois, not fast.
Ps cumidine	1 : 2 : 4 : 5	Flesh colour, not fast.
Isoduridine	1 : 2 : 3 : 5 : 4	Light mode, not fast.

These experiments show that aniline alone gives a fine black,

and that the presence of the methyl group in the ortho position does not greatly modify the shade unless it be by clearing it (*o*-toluidine), whereas the methyl group in the meta position gives a violet shade and in the para a loose brown shade. The bases which contain CH_3 in the ortho or meta position give maroons, greys and similar shades. The *o* and *m*-toluidines may be differentiated by these dyeings. The methyl group in para in the amine group do not give dyeings fast to soaping.

In the same order of ideas Rettig also tried the aminophenols and *o*-aminophenetol, using 4 grammes of hydrochloride per litre of bath, obtaining the following results:—

O—aminophenol	1 : 2	Blue-black.
M—aminophenol	1 : 3	Light bistre.
P—aminophenol	1 : 4	Dark bistre.
O—aminophenetol	1 : 2	Dark catch.

All were sufficiently fast to soaping. The hydroxyl group in para in the amino group does not prevent the production of fast dyeings.

Monnet (*D.R.P.* 37,661) oxidised a mixture of paraphenylenediamine and aniline.

Dreher (*D.R.P.* 127,361) oxidised a mixture of *m*-nitraniline and aniline.

Reisz (*B.F.* 243,554—*D.R.P.* 134,559) reserved to himself the right to oxidise aromatic compounds containing an amine group. Bismarck Brown oxidised under the same conditions as aniline gives a catch brown. The process is of no commercial value, and the German patent is void.

Binder (*B.S.M.*, 1895, p. 29) obtained a brown by the action of benzidine on manganese bistre.

Scheurer, using dianisidine, also obtained a brown.

Paraphenylenediamine has recently found varied and important uses. Henri Schmid has produced with it the fast colour known as Paramine Brown (*D.C.P.*, 1906, p. 25).

The list of researches on the oxidation of the various basic bodies of the aromatic series is completed by the work of E. Ulrich and V. Fussganger (*B.S.M.*, 1902, p. 264) on the oxidation of the derivatives of diphenylamine.

These chemists found that *p*-amino *p*-oxydiphenylamine, *p*-aminodiphenylamine, *p*-aminomethyldiphenylamine, diaminodiphenylamine, and dimethyldiaminodiphenylamine, give an intense and absolutely ungreenable black by oxidation on the fibre.

These bases oxidise so easily that it is not necessary to use a catalytic agent, the colour develops on drying the fabric on the drums. Meister, Lucius and Bruning have patented the result of these researches, and para-aminodiphenylamine is on the market under the name of Diphenyl Black Base (*D.C.P.*, 1902, p. 132).

CHAPTER II.—Theory of the Formation of Aniline Black.

Aniline black is obtained from aniline by elimination of the hydrogen. This can be effected by various oxidants, for instance, the compounds of chlorine with oxygen, chromic acid, ferric salts, or peroxide of manganese. Chloric acid does not transform aniline into the black; there is no formation of aniline black when a solution of chlorate of aniline is boiled. The moment, however, that a drop of another acid is added or a small quantity of a metallic salt, forming a chlorate which is easily dissociated, such as a salt of vanadium, copper, manganese or iron is introduced, the black appears. The chloric acid is then decomposed, and it is the products of this decomposition that oxidise the aniline.

Lightfoot's experiments gave birth to the long held belief that the presence of a metal capable of a high degree of oxidation was indispensable to the production of the black. It was thought that the chlorate brought the metal to its highest degree of oxidation, that this derivative in its turn gave up its oxygen to the aniline, then was re-oxidised by the chlorate, and so on in a cycle. This theory was sustained by a large number of chemists, and was developed by Antony Guyard in particular (*B.S.C.P.* xxv., p. 58).

Rosenthal (*B.S.M.*, 1876, p. 179) showed, however, that the metallic salt decomposes the chlorate and that the chlorine, and particularly its compounds with oxygen, transform the aniline first into emeraldine, then into black.

By a laborious research he proved, beyond the shadow of a doubt, that the compounds of chlorine with oxygen produce the black, without the intervention of the slightest trace of a metal.

The electrolytic experiments of Coquillion and of Goppelsroeder also proved that the production of the black is possible without the assistance of a metal.

Nevertheless, we do not regard the theory based on the action of metals at a high degree of oxidation as entirely erroneous. From our point of view either reaction may be admitted, according to the special circumstances of working. When aniline is oxidised in the presence of cupric chloride, and of an *insufficient* quantity of chlorate, it will be found that when the black is produced it is in mixture with cuprous chloride (Nietzki, "*Matières colorantes organiques*," 1901, p. 252).

Nietzki (*Ber.* ix., p. 616) analysed the black prepared by Armand Muller's method. The crude product was washed several times in

boiling hydrochloric acid, dried, powdered, and treated successively with benzole, ether, petroleum ether and alcohol. Nietzki found later that repeated treatment with alcohol, saturated with hydrochloric acid is sufficient. The residue is a dull, dark green powder. Alkalis change it to a violet, which takes a bronze reflex on drying. Heated alone or with soda lime, the aniline black gives on distillation a liquid with a basic reaction, containing a large proportion of aniline. The hydrochloride dissolves in aniline, and the base even more easily. Hydrochloric acid separates the hydrochloride from the black; nevertheless, a good part of it remains in solution. Analysis of the hydrochloride dried at 100° C. gave:—

C ...	68.29	68.95	69.15	—	—	—	—
H ...	4.90	5.10	5.25	—	—	—	—
N ...	—	—	—	13.65	—	—	—
Cl ...	—	—	—	—	11.64	11.84	11.88

Nietzki deduced from this the formula $C_{18}H_{15}N_3HCl$, corresponding to 69.70 C—5.17 H—13.59 N—11.47 Cl.

When the black is heated for several hours in a water-bath with fuming sulphuric acid, then poured into water, a precipitate similar to the original black is produced, insoluble in dilute sulphuric acid, but, on the other hand, soluble in water to a dark green solution. The salts are amorphous; the soda salt is soluble in water, the salts of barium and of silver insoluble. This body is without a doubt a sulphur derivative of the black.

The violet colour of the solution of the black in concentrated sulphuric acid becomes, a yellowish brown on the addition of nitric acid. Water separates out a light brown body soluble in alkalis, and in alcohol to a dark yellow solution. On oxidation by means of bichromate of potash and an excess of sulphuric acid, aniline black is dissolved with the production of a notable quantity of quinone.

Goppelsroeder gave the hydrochloride of aniline black the formula $C_{24}H_{20}N_4HCl$, Kayser wrote it $C_{12}H_{10}N_2HCl$.

In another article (*Ber.*, ix., p. 1.093) Nietzki returns to the question of the formula of aniline black. If it is extracted with acid, the black contains carbon, hydrogen and nitrogen in the proportion of 6:5:1. It thus constitutes a molecule of aniline robbed of two atoms of hydrogen, and its formula would be a polymer of C_6H_5N . The divergences in the calculation of the chlorine are explained by the fact that the hydrochloride is easily split up by drying. Nietzki found in the electrolytic black dried at 100° C. between 11.6 and 11.8 per cent. of chlorine; when the temperature reached 110, 140 and 160° C., the percentage fell to 9.4, 8.3, and 5.5, respectively.

Kayser, who had also noted this, treated the salts before analysis with an excess of acid, and then washed them in alcohol and ether. He then found 15 and 16 per cent. of chlorine.

Nietzki, by operating in this manner, but finishing by drying in a vacuum, obtained only 13 to 14 per cent. of chlorine. By a series of experiments he determined the maximum quantity of acid that aniline black can fix. He set a given weight of the base to digest in an alcoholic or aqueous solution of hydrochloric acid, and then titrated the excess of acid in the liquid. He found 13.8, 13.5, 13.2, and 13.7 per cent. The bi-hydrochloride of a base $C_{30}H_{25}N_5$ corresponds to a content of 13.4 per cent. This proportion corresponds so well with those found that this formula may be looked upon as being really that of the black.

With sulphuric acid he found 23 and 22.9 per cent. The neutral sulphate, $C_{30}H_{25}N_5H_2SO_4$, corresponds to 17.7 per cent., and the acid sulphate, $C_{30}H_{25}N_5(H_2SO_4)_3$, to 24.4 per cent. The chloroplatinate does not give constant results, they vary between 19 and 22 per cent. of platinum.

If aniline black is heated with acetic anhydride, a light grey powder is obtained, which is insoluble in aniline and also in sulphuric acid. Analysis gives figures which may be represented by the formula $C_{30}H_{23}N_5(C_2H_3O)_2$.

The action of certain reducing agents on aniline black is interesting to study. When the finely powdered base is heated with potash in alcoholic solution and zinc dust, the mass is decoloured by the formation of the leuco base, which is just as insoluble as the black itself. The colouration returns instantaneously on contact with the air.

On boiling with tin and hydrochloric acid or acid stannous chloride, a bluish green body is obtained, which slowly becomes green, but is turned rapidly to a blue black by the action of alkalis. By consecutive treatments with tin and hydrochloric acid or hydriodic acid ($Sp.G=1.7$) and with white phosphorus, phenylenediamine, $C_6H_4(NH_2)_2$ and diparadiamino diphenylamine $NH(C_6H_4NH_2)_2$ are obtained in addition to resinous substances. When the base of the black or one of its salts is treated with bichromate of potash, a violet black is obtained which dilute acids do not turn green. This body has a great resemblance to the original black, but after grinding shows a brilliant metallic green. This compound appears to be chromate of aniline black, as it yields either by calcination or by titration with sulphuric acid 8.19 to 8.33 per cent. of CrO_3 . Nietzki considered this to be the type of industrial aniline black; as we shall see later, this opinion was not verified. In another article (*Ber.* 1884, p.226) Nietzki wrote that he had obtained an aniline black with the probable formula $C_{18}H_{15}N_3$ by oxidising diparadiaminodiphenylamine, in still more abundance by oxidising a molecule of this base and a molecule of aniline, and finally by oxidising equal molecular weights of paraphenylenediamine and diphenylamine.

By heating acetate of aniline black with 8 to 10 parts of aniline at from 150 to 160° C. for six to eight days, pouring the result into water acidulated with hydrochloric acid and filtering the hydro-

chloride formed, Nietzki obtained a new and different base of the black, of which the hydrochloride, insoluble in water, dissolves in alcohol, from which it crystallises out in coppery needles. The alcoholic solution of the hydrochloride is blue, alkalis turn it to a beautiful crimson. The solution of the base in ether is a fine magenta red colour. The base itself is blue and is insoluble in water and the usual solvents. The alkaline solution of the base, and also the neutral solutions of the salts, are discoloured by boiling with zinc dust; the colour instantaneously re-appears on contact with the air. The acid solutions are also decoloured by zinc dust. Concentrated sulphuric acid dissolves this new body to a blue solution, and on heating forms the sulphur compound. Nitric acid dissolves it without modifying the colour, but decomposes it on heating.

Analysis of the base and its salts led Nietzki to assign to it a formula approaching $C_{36}H_{33}N_5$ or $C_{36}H_{34}N_5$. Subsequent analyses seemed to warrant the more exact formula $C_{36}H_{29}N_5$, making it appear that this body results from the condensation of a molecule of the black and a molecule of aniline, with elimination of ammonia. Nevertheless, it is unlikely that it is a phenyl black; its properties and its composition seem to range it among the indulines.

Antony Guyard (Hugo Tamm) (*B.S.C.P.* 1876, p. 58) showed that aniline black is produced by the action of a trace of a vanadium salt in a mixture of hydrochloride of aniline and chlorate of potash or soda. One cc. of a very dilute solution of chloride of vanadium or vanadate of ammonia is added to a mixture of 100 grammes of water, 8 grammes of hydrochloride of aniline, and $3\frac{1}{2}$ to 4 grammes of chlorate of potash or soda. The liquid darkens in a few moments, and at the end of 48 hours it has become a thick mass of aniline black. One part of chloride of vanadium is sufficient to transform 1,000 parts of the aniline salt into black.

Witz (*B.S.R.* 1876, p. 315) asserts that one part of vanadium will transform 270,000 parts of aniline salt into black if sufficient chlorate is used.

Nietzki (*Ber.* xi., 1907) obtained a substance analogous to aniline black by oxidising ortho-toluidine under similar circumstances to aniline. This body is only slightly soluble in alcohol, and dissolves easily in chloroform and aniline. The base is violet, the salts green. The formula of the base is C_7H_7N . Acids precipitate it from its solution in chloroform.

Kayser (*W.J.*, p 977) analysed four aniline blacks obtained by different methods.

1. Twenty grammes of hydrochloride of aniline, 10 grammes of chlorate of potash, 240 cc. of water, and 20 centigrammes of vanadate of ammonia give a greenish black paste. This is filtered, washed with boiling water, dried and extracted with alcohol as long as the liquid takes a yellow tint. The filtrate contains a large proportion of free hydrochloric acid. The precipitate is then treated with a 2 per cent. solution of soda, then with water, and

finally once more with alcohol. A voluminous violet blue powder is thus obtained; it takes a metallic lustre on rubbing, leaves no ash, and is free from chlorine. Analysis assigns it the empiric formula C_6H_5N .

Calculated.				Found.			
C	...	79.12	...	78.80	79.02	78.16	—
H	...	5.49	...	5.81	5.65	5.8	—
N	...	15.38	...	—	—	15.75	15.03

The black thus obtained has slightly basic properties. It dissolves in sulphuric acid to a violet solution; water throws the sulphate down from this in a flocculent green precipitate. Creosote, aniline and melted phenol dissolve it to a dark blue solution; the solution in aniline rapidly turns brown. If 3 to 4 volumes of alcohol (Sp.G=0.83) are added to the solution in creosote or phenol, a dark indigo blue precipitate is obtained. The blue solution is decoloured by hydro-sulphide of ammonia and turned green by acids. The salts of the black base are decomposed by water, and still more rapidly by acids.

Kayser found in the hydrochloride a content of acid corresponding to $C_{12}H_{10}N_2$, HCl , and in the sulphate $C_{12}H_{10}N_2$, H_2SO_4 . As already pointed out, Nietzki thought that these salts retained a certain quantity of acid.

2. Kayser's second black, prepared by Armand Muller's process, has the same properties as No. 1, and gave on analysis:—

C	78.80	77.95	—	—
H	5.34	5.77	—	—
N	—	—	15.30	15.26

3. The third black was prepared by leaving for some time, at the ordinary temperature, a mixture of 20 grammes hydrochloride of aniline, 40 cc. of water, and 60 cc. of 32 per cent. hydrochloric acid. The black completely separated out at the end of four days, and had the same properties and the same composition as Nos. 1 and 2. Analysis gave:—

C	78.48	78.23	—	—
H	5.75	5.57	—	—
N	—	—	15.69	15.19

4. The fourth black was produced by boiling 40 grammes of ferro-cyanide of aniline and 10 grammes of chlorate of potash in 220 cc. of water. Hydrocyanic acid gas is evolved, and a black precipitate is formed, which was washed in water and alcohol. Alcohol extracts a fairly large quantity of a brown red substance, and a black mass finally remains which in a large measure dissolves in creosote, phenol and aniline. This colour is not changed by the action of alkalis, *nor yet by the action of acids*. This ferro-cyanide black is therefore clearly differentiated from Nos. 1, 2, and

3, which seem to resemble each other. Kayser does not give the analysis of No. 4. Liechti and Suida (*M.T.G.W.*, 1884, p. 21) studied the aniline black formed by the spontaneous decomposition of the chlorate. This salt is obtained by adding a molecule of sulphate of aniline to a cold saturated solution of a molecule of chlorate of barium. The mixture is stirred until no more precipitate is produced. In a short time, white prisms, 3 to 5 centimetres long by 2 to 3 millimetres thick, appear. These crystals do not change so long as they are left in the liquid, but very rapidly turn a blue-black when exposed to the air, and at the same time take a metallic lustre. In a few moments they decompose with a bright flame, giving off abundant aromatic and suffocating vapours. When the crystals are exposed to the air while still wet they turn black, and if they are moistened from time to time, and thus prevented from deflagrating, they are transformed entirely into black and preserve their form without alteration. This is a highly interesting case of pseudomorphosis.

The reactions of the chlorate of aniline solution are as follow:—The solution may be heated to boiling point without decomposing, but if hydrochloric acid, ferric chloride or chloride of vanadium is added to the boiling solution there is an abundant formation of the black. When the solution is decomposed with dilute sulphuric acid it yields little emeraldine under the action of heat and turns a dark violet, on cooling it becomes brown. When sulphate of copper is added to the solution it simply turns brown on heating, but hydrochloric acid throws down from this an abundant black precipitate. Tartaric and acetic acids are without action, even on boiling; if ferric chloride is added very little emeraldine is formed, but the solution turns a deep brown and finally a brown colour separates out.

Chlorate of aniline solution may be boiled for a long time with dilute nitric acid without changing; the addition of ferric chloride determines a violent reaction, accompanied by the formation of a blue precipitate, which turns green, whereas the liquid takes a red colour. If bichromate of potash and sulphuric acid are added to the solution the black is formed quickly and in abundance. When heated with hydro-chloride of ammonia the solution is not changed; the addition of sulphate of copper causes the immediate formation of the black, and at the same time the red colouration of the liquid. Boiled with vanadate of ammonia the solution takes a brown tint and eventually gives a brown deposit; this is soluble in alcohol, and does not turn black on the addition of hydrochloric acid. When heated with hydrochloride of aniline it is not modified. When it is decomposed in cold hydrochloric acid, a large quantity of emeraldine forms at the end of 24 hours, and the supernatant liquid takes a brown colour. If after filtering the filtrate is heated a fresh quantity of emeraldine is obtained, and a brown substance soluble in ether separates out. On filtering once more and evaporating the violet liquid obtained, more black separates

out; hydrochloride of aniline, sal ammoniac, and a substance which gives the strong odour of isonitrile on boiling with caustic potash, can be extracted from the dried product by means of water.

The black crystals obtained by the transformation of chlorate of aniline are washed in cold water, then in boiling water, next in dilute hydrochloric acid, alcohol and ether. They are then splendid prisms of a lustrous steel blue; they are the hydrochloride of the base thus formed. As shown by analysis, the base itself contains chlorine; its formula corresponds to $C_{18}H_{14}ClN_3$.

<i>Calculated.</i>			<i>Found.</i>			
C ...	70.2		70.59	69.44	—	—
H ...	4.6		5.72	4.86	—	—
Cl ...	11.5		—	—	12.01	12.05
N ...	13.7		—	—	—	13.11

The black obtained in this manner is therefore differentiated by its chlorine from the blacks analysed by Nietzki and Kayser. There is nothing surprising in this in view of the fact that this black is formed by a molecule of chloric acid and a molecule of aniline, whereas the chlorate black of Nietzki and Kayser only requires one molecule of chlorate to two molecules of aniline.

The blacks of Liechti and Suida, those of Nietzki and Kayser and the electrolytic blacks of Goppelsroeder and Coquillion are very similar in their properties. Liechti and Suida by treatment of their black, either the base or the hydrochloride, with bichromate of potash obtained a bronze powder, which left after incineration 11.47 to 11.68 per cent. of Cr_2O_3 . The chromium contained in the powder is, in part at least, in the state of chromic acid. By heating the hydrochloride of their black for two minutes with a solution of chromic acid, 2 grammes per litre, Liechti and Suida obtained an intense black in brilliant crystals, giving on incineration 10.75 to 11.81 per cent. of oxide of chromium, but the chromium in this case is not contained in the state of chromic acid, but as oxide of chromium, a treatment with hydrochloric acid in fact extracts all the chromium from the product. This black also contains chlorine and in addition to this oxygen. Analysis shows:—

C ...	55.87
H ...	6.25
N ...	10.48
Cr ...	8.09
Cl ...	6.15
O ...	13.16 (calculated by difference).

The oxygen must be calculated as 9 per cent. if the chromium is calculated in the state of free chromic acid. This analysis shows that the black is oxidised by the chromic acid, and that at the same time a part of the chlorine is eliminated. If the black is boiled for an hour with a weak solution of chromic acid it absorbs still more chromium, i.e. 15.02 per cent.

The primitive basic black, which produces green salts with the

acids, becomes acid on treatment with chromic acid, and the acids no longer turn it green. The oxidised black after its formation has alone the property of fixing chromium. A black prepared with hydrochloride of aniline, bichromate of potash and acid in the proportion necessary to produce the compound $C_{18} H_{15} N_3 H Cl$, does not contain after washing more than 0.16 per cent. of $Cr_2 O_3$.

Liechti and Suida's black after boiling for two minutes with a very dilute solution of chloride of lime, followed by washings in water, hydrochloric acid and again in water, then dried at $105^\circ C$. showed on analysis the following composition:—

C	...	62.58
H	...	6.16
N	...	12.65
Cl	...	8.66
O	...	9.85

As will be noted, this product also contains oxygen. Like the product superoxidised with chromic acid this body is not modified by acids. Liechti and Suida gave to their black the name of Emeraldine, although it is certainly not identical with the body already called by this name. By distillation with zinc dust they extracted from it diphenylene diamine $C_6 H_5 NH-C_6 H_4-NHC_6 H_5$. The point of fusion of the base is $140^\circ C$., of the diacetyl derivation 170 to $172^\circ C$., of dinitrosamine 108 to $110^\circ C$. They also obtained diparadiaminodiphenylamine, a small quantity of paraphenylenediamine, aniline and ammonia.

Calm (*Ber.*, xvi. p. 2,799) obtained a diphenylparaphenylenediamine. In spite of a notable difference in the melting point, this body seems to be identical with that obtained by Liechti and Suida.

Noelting and Jules Brandt, in a hitherto unpublished research, made comparative trials of various aniline blacks obtained by different methods. They have not yet made precise experiments with the oldest known aniline black, the by-product of the manufacture of mauveine. It is the result of the oxidation of aniline by bichromate and is ungreenable. One hundred grammes of aniline are dissolved in a litre of water, and 200 grammes of concentrated sulphuric acid and this solution is added to another containing 300 grammes of bichromate of potash in two litres of water. After the cold mixture has been left for 48 hours the aniline black which has separated out is freed by alcohol from the violet colouring matter which accompanies it, then washed with warm dilute sulphuric acid until the acid leaves no residue on a platinum foil. The aniline black is then in the form of a black powder, soluble in concentrated sulphuric acid to a violet solution, and giving 0.67 per cent. of ash. Three analyses of this product, washed once with alcohol and distilled water, gave per cent.:—

C	...	64.35	63.25	62.90
H	...	5.30	4.94	4.40
N	...	10.00	10.24	?

The black, therefore, contains a notable proportion of oxygen.

As a second bichromate black, that described by Glanzman (*B.S.R.*, 1874, p. 121) was selected. Eighty grammes of bichromate of potash were dissolved in a litre of water, and 100 grammes of aniline were added. Then 100 grammes of hydrochloric acid at 22° B. diluted with 400 c.c. of water were added gradually, heating to about 50° C., then the mixture was brought to the boil and kept at this temperature for two hours. Half the oxidation product thus obtained is soluble in alcohol; the residue contains 45 per cent. of oxide of chrome and therefore Glanzman's process gives a very poor yield of aniline black.

Armand Muller's black was next prepared. It was treated with alcohol and hydrochloric acid and heated with concentrated ammonia until the chlorine completely disappeared. After washing with distilled water a bronze powder remained, which, in two analyses, gave 13.28 and 13.38 of nitrogen.

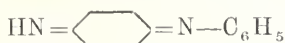
These figures do not agree with those obtained by Nietzki with the hydrochloride, and by Kayser with the free base of an aniline black prepared in the same way. The product still contained chlorine, whereas that analysed by Nietzki no longer contained it. The chlorine cannot be extracted either by digestion in alkalis or by solution in cold sulphuric acid at 66° B., and this confirms the observations of Liechti and Suida touching the production of aniline black by the spontaneous decomposition of chlorate of aniline. In this case also a part of the chlorine is not dissolved in concentrated sulphuric acid. By treatment with hot concentrated sulphuric acid, Noelting and Brandt obtained an abundant evolution of hydrochloric acid vapours, characterised by nitrate of silver. It is thus proved that the chlorate, according to circumstances, may either oxidise or chlorinate.

Noelting and Brandt finally tried an aniline black prepared in the manner pointed out by A. Riche in his work as an expert in connection with a Grawitz law-suit. Fifty c.c. of ferric chloride at 43° B. and 20 c.c. of aniline were dissolved in 100 c.c. of water, and to this was added a solution of 23 grammes of chlorate of soda in 100 c.c. of water. The mixture was then heated gently. The black formed contained a considerable quantity of iron, which, according to Riche, could not be eliminated without decomposing the black, but which has easily been extracted by Noelting and Brandt by repeated washings with dilute hydrochloric acid. Analysis of the product, carefully purified in boiling water and alcohol, gave 0.3 per cent. of ash, and in three analyses 10.27, 10.45 and 10.17 per cent. of nitrogen. Riche's black appears to contain oxygen, but it is less rich in nitrogen than that of Armand Muller.

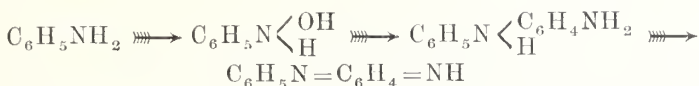
Comparative tests, therefore, show that the composition of aniline black varies with the method of preparation.

Caro, long ago, made the observation that the manipulated oxidation of aniline in cold alkaline solution gave azobenzole and a product soluble in water to a pure yellow solution which is transformed by acids into an insoluble green, with essential properties

resembling those of emeraldine prepared by oxidising aniline in the presence of acid. Caro (*I.G.D.N.A.*, 1896, p. 119) succeeded later in collecting the yellow resulting from the oxidation of aniline from its generator, paraminodiphenylamine, and extracting it afresh in crystals by oxidation. This yellow oxidation product has evidently the constitution of a phenyl-paraquinondiimine.



According to Bamberger and Tschirner (*Ber.* xxxi. p. 1,512), who studied the oxidation of aniline and other analogous bases, its formation is explained as follows:—



Persulphates in acid solution oxidise aniline, producing emeraldine. Caro (*Z.A.C.* 1898, p. 845) states that if concentrated sulphuric acid is saturated with persulphate of ammonia or potash, and this solution is poured into a solution of aniline in water, nitroso benzole is obtained by neutralisation. Caro was not able to discover how the persulphuric acid, or its decomposition products, acted, but he obtained the same result by the action of persulphate dissolved in concentrated nitric acid, and also by electrolysis of sulphuric acid of 45° B. Baeyer and Villiger have since studied this product, which they term Caro's re-agent, or hypersulphuric acid. It is a product which may find interesting applications, but has not been found of service in the production of aniline black.

E. Boernstein (*Ber.* xxxiv., p. 1,284) by fusing aniline black with potash, obtained paradiphenylphenylenediamine, which had been obtained by Liechti and Suida by distilling aniline black with zinc dust, and a violet substance insoluble in benzol, but soluble in concentrated sulphuric acid to a dark green solution, and in dilute acid to a blue, changing to violet. This body is easily soluble in alcohol, acetone and chloroform; it is decoloured by reduction with zinc and acetic acid.

E. Knecht (*J.S.D.C.* 1897, p. 1,419), in his observations on the production of aniline black on nitrated cotton, brings forward a new instance of the formation of aniline black without the intervention of a metal.

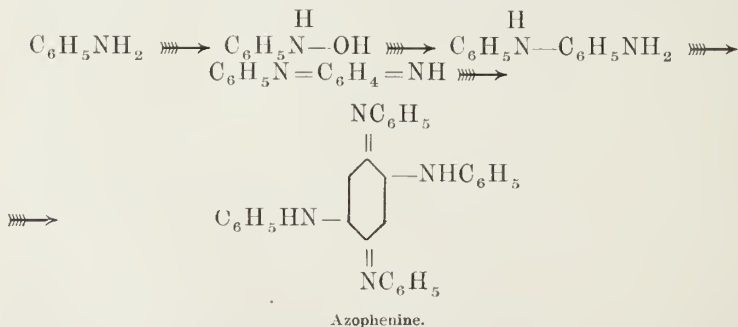
Like the chlorate, bichromate of aniline in a pure state is relatively stable; but the least addition of acid to the solution determines the formation of aniline black. The black produced *in vitro* is also produced on the fibre. Numerous processes of reserve under aniline black are based upon the principle, *without acid no black*. Prud'homme's elegant process, to which we shall return later, is an interesting application of this law.

Aged aniline black is usually distinguished from direct black. This distinction might lead to the belief that there is a very

complete difference between the two blacks; in our opinion this is not the case. Ageing in the air merely allows the oxidant sufficient time to exercise its action; the solution, which contains all the elements necessary to the formation of the black, is concentrated by evaporation of the water, and the oxidation spreads by degrees into the interior of the fibre. The oxygen of the air also seems to play an important part. Ageing can be replaced by an elevation of temperature. Thus Lightfoot's black and the vanadium black, which require an exposure of two or three days in the air, can be developed in a minute or two in the steaming chamber.

Unfortunately the chemical mechanism of the production of the black is not yet thoroughly determined. As the researches of Nietzki, Kayser, Liechti and Suida, Noelting and Brandt, and many other chemists, have demonstrated, different oxidation products of varying composition are obtained, according to the processes employed. In all cases the lower oxidation products behave like bases, but their salts are unstable and difficult to produce with a constant content of acid. The higher oxidation products, on the other hand, are capable of combining with metallic oxides and of containing oxygen, as analysis shows, and are thus phenolic or acid. In addition, the blacks obtained with an excess of chlorate contain chlorine which cannot be eliminated by the alkalis.

Bamberger and Tschirner (*Ber.* xxxi., p. 1,527) have lately sought to determine the phases aniline passes through until it arrives at its highest degree of oxidation, nigraniline. According to these chemists, the first product of oxidation is phenylhydroxylamine which, following Bamberger and Lagutt, is condensed with a second molecule of aniline to form phenylparaquinonediimine. The diimine can, by the addition of a further three molecules of aniline, be transformed into dianilidoquinonedianile, known as azophenine, the product used in the manufacture of the indulines.



Direct oxidation of aniline produces a complex molecule containing 30 atoms of carbon. Carrying the oxidation further, and arriving at the formation of aniline black, the process passes through one or other of the phases indicated above and the method of oxidation has a determined influence on the formation of the black, the nature of which we cannot decide at present.

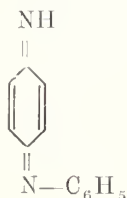
R. Vidal (M.S. 1902, p. 218) proposed the formula:—



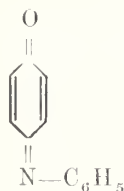
This evidently does not represent the black, but its leuco derivative, and moreover cannot be applied to the ordinary black free from oxygen. Leaving out the hydroxyl, it coincides with the first formula of R. Willstaetter for leuco-emeraldine. (See p. 34.)

The theory of Bamberger and Tschirner is fully confirmed by the researches of Ulrich and Fussgaenger on the production of aniline black. These researches are not only interesting, but of practical importance.

The recent researches of Willstaetter and Moore (*Ber.*, 40, 2,666, 1907) have finally shown the route by which, commencing at aniline, we can gradually arrive at the black, passing by a series of well characterised and crystallisable intermediate products. As point of departure, these chemists have taken the oxidation product of aniline obtained by Caro, which he considered to be phenolquinonediimine.

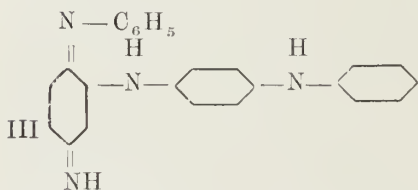
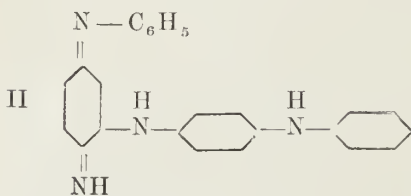
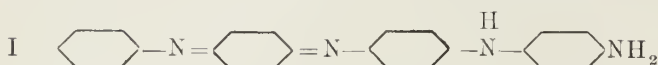


He showed that this body is a mixture of equal parts of this diimine and of the phenylquinonemonoimine of Bandrowski.

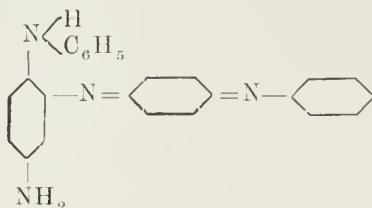
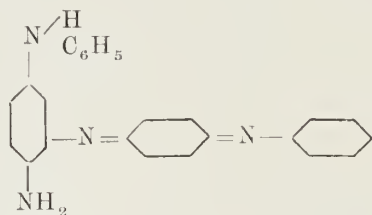


The pure diimine is easily obtained by oxidising by means of oxide of silver, a solution of paraminodiphenylamine in ether. It takes the form of yellow prisms, fusible at 88 to 89° C. In the presence of water it very easily changes to monoimine, which, with a molecule of the original product, forms Caro's compound, fusible at 73 to 77° C. By the prolonged action of the water, it changes entirely into monoimine. Under the influence of diluted acids, diimine changes almost instantaneously into emeraldine. Its hydrochloride also undergoes the same transformation, but less

rapidly. Three formulæ are possible for emeraldine, $C_{24}H_{20}N_4$:—



By altering the position of the quinone group three other very analogous formulæ are obtained:—



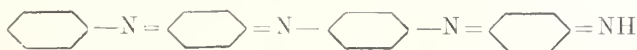
Emeraldine is still more easily produced by oxidising paraminodiphenylamine in acid solution by means of perchloride of iron or peroxide of hydrogen in the presence of a little ferrous sulphate. The yield of pure product, separated from the black simultaneously formed by means of boiling benzole, is from 70 to 80 per cent. of the theoretical yield. The elementary analysis corresponds to the composition C_6H_5N , and the cryoscopic determination of the molecular weights shows it to be $C_{24}H_{20}N_4$. The product directly obtained is amorphous; in order to crystallise it the best way is to reduce it to begin with to the state of leuco base, $C_{24}H_{22}N_2$, and to oxidise this in solution in acetone by means of oxide of silver. Emerald-

dine then presents itself in the form of microscopic blue needles. It is easily soluble in acetone and chloroform, with difficulty in alcohol, ether, and cold benzol. The alcoholic solution is blue, the benzol solution is cherry coloured. Aniline dissolves it to a blue solution, concentrated sulphuric acid to a red carmine. It is a strong base, the salts are green, and only slightly soluble in water.

The leuco base is easily produced by the action of reducing agents; phenylhydrazine in particular gives a good yield of pure product. A polymer of the black is also produced simultaneously with the leuco base by heating emeraldine in water for five hours at 150 to 170° C.



The leuco base crystallises out of alcohol in beautiful white needles, fusible about 185° C. It is very easily soluble in acetone, with difficulty in cold alcohol and benzol, more easily if these are heated, with difficulty in ether. Oxidants transform it to begin with into emeraldine, and next into a red imine $C_{24}H_{18}N$. This imine is more simply obtained by oxidising emeraldine in solution in benzol by means of dioxide of lead. It forms crystalline red plates, fusible at 195 to 196° C., and forming a polymer of the black. It is very difficult to dissolve it in alcohol, ether or acetone. It is dissolved with difficulty in cold, easily in hot, benzol, and also in chloroform. The solution in concentrated sulphuric acid is red violet, bluer than that of emeraldine. It forms salts, but these are easily transformed into quinone. Adopting for emeraldine the first formula on page 34, the imine will be



By polymerism the imine easily becomes a black, which seems to be identical, or at least very analogous, with the aniline black obtained by the processes of Armand Muller and Nietzki. The best means of bringing about the polymerism is to heat the finely divided imine with 100 times its weight of water for four hours at 150 to 170° C. Analysis proves it to correspond to the formula $(C_{24}H_{18}N_4)_x$.

				Theoretical.		Found.
C.	79.50	...	79.71
H.	5.01	...	5.02
N.	15.49	...	15.19

The figures found by Muller and Nietzki correspond with this formula just as well as with that richer to the extent of two atoms of hydrogen $(C_{24}H_{20}N_4)_x$ or $(C_6H_5N)_y$, which is generally admitted. It follows that on oxidation a molecule of aniline abandons not two, but two and a half atoms of hydrogen. This black is insoluble in the usual solvents, very slightly soluble to a reddish violet solution in concentrated sulphuric acid, very slightly also in phenol,

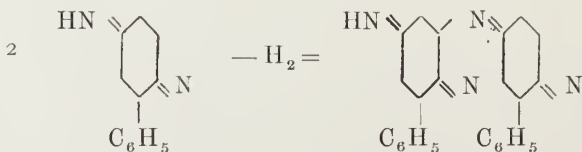
aniline, nitro-benzol, and hot naphthalene. Sulphuric acid has no effect on it; it seems from this that the ungreenable blacks still contain emeraldine, and we have in this case an ungreenable black containing neither oxygen nor metallic oxide and distinguished by this from those already noted. The hydrochloride corresponds to the formula $(C_{24}H_{18}N_4HCl)_x$; this is a molecule of hydrochloric acid to four molecules of aniline.

Sulphuric acid at 16° B. does not attack the black even on boiling, but a mixture of bichromate and sulphuric acid transforms it into quinone.

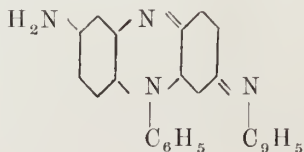
By heating the red imine with water simply to the boiling point, another black is formed more soluble in the usual solvents than the preceding one or than the ordinary oxidation black. Very dilute cold sulphuric acid transforms the imine into again a different black, containing oxygen; at the same time emeraldine is formed, and a red imine combined with oxygen. This same imine, $C_{24}H_{17}ON_3$, is also formed in small quantity by the side of the imine $C_{24}H_{18}N_4$, when emeraldine in solution in benzol is oxidised. It is separated out by taking advantage of its less basic properties. It melts at 216 to 217° C. without alteration, and on reduction gives a leuco base $C_{24}H_{19}ON_3$, fusible at 194 to 195° C., and by polymerism a black containing oxygen, soluble in concentrated sulphuric acid to a pure blue solution, almost insoluble in boiling aniline.

A blue imine containing oxygen, analogous to emeraldine, $C_{24}H_{19}ON_3$, is obtained by oxidising equal molecules of paramino- and of paroxy-diphenylamine with peroxide of hydrogen in the presence of ferrous sulphate. It crystallises in blue needles, fusible at 148 to 149° C. The corresponding leuco base melts at 198 to 200° C., and by oxidation gives a red imine fusible at 222 to 223° C. This last gives a black by polymerism. The isomerism of these two derivatives is not yet explained.

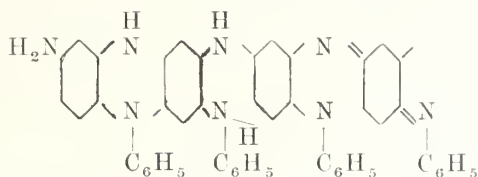
Bucherer (*Ber.* 40, 2,412, 1907) takes a rather different view of the formation of the imines and of the black; his theory is explained by the following formulæ:—



This product is transposed into:—



This body has at one and the same time the character of an amine and an imine, and by polymerism gives:—



This derivative has 48 atoms of carbon. By the fresh addition once or twice of C_{24} , more condensed blacks, C_{72} and C_{96} , may be obtained.

These formulæ do not take properly into account the transformation, quantitative, so to speak, of the black into quinone. The first formula of Willstaetter seems to us more probable.

CHAPTER III.—Processes to Obtain Ungreenable Aniline Black.

By the action of oxidants on aniline a series of different products is formed. These may be divided into three classes:—

1. The less oxidised bodies. The chief of these is emeraldine, which is blue in the basic state and a bright green when combined with acids. It is with difficulty, and only partially, soluble in alcohol, crystallisable acetic acid, aniline, and phenol. Concentrated sulphuric acid dissolves it to a reddish violet solution. This product is probably identical with that which results from the manipulated oxidation of a molecule of paraphenylenediamine and a molecule of diphenylamine or of equal molecular weights of paraminodiphenylamine and aniline.

The composition of emeraldine has been established by Willstaetter. It is probably never obtained in a pure state from aniline, but always in mixture with nigraniline.

2. By continuing the action of an oxidant on this emeraldine, aniline black is obtained, called nigraniline by Rheinick, and polymerised black by Willstaetter.

Nigraniline is insoluble in the usual solvents, it is slightly soluble in aniline and phenol to a dark indigo blue (rather reddish) solution. Its salts are also green, but less bright than the salts of emeraldine. Analyses of nigraniline made by Nietzki, Kayser and Goppelsroeder show it to correspond to a polymer of C_6H_5N , but Willstaetter has shown that it contains less hydrogen and that the formula should be $(C_{12}H_9N_2)_x$. Liechti and Suida have obtained a nigraniline containing chlorine, as we have already stated. Nigraniline constitutes the major part of ordinary black. This is admitted without dispute, and it is also found in the less oxidised products—emeraldine, for instance. Acids, and in particular sulphuric acid, turn nigraniline green. This acid acts as an energetic reducing agent, and without doubt leads the nigraniline back, all or in part, to the state of emeraldine.

3. Finally, ungreenable black is the product of a still higher state of oxidation. It is formed by the oxidation of nigraniline in the presence of heat, but under certain conditions it also forms without an elevation of temperature. It does not green under the action of acids, not even sulphuric acid, very probably because it does not form salts. Acid tinsalt reduces it to the leuco base, and this on oxidation becomes ungreenable black again.

Leichti and Suida, and also Noelting and Brandt, have analysed ungreenable aniline black. According to their analyses, this black contains oxygen, and is capable of combining with metallic oxides — oxide of chromium, for instance. Glanzmann's ungreenable black also contains this oxide. On the other hand, Leichti and Suida's experiments show that the presence of a metal is not indispensable to the formation of ungreenable black, whether as a precipitate or on the fibre. These chemists have obtained it by oxidising the nigraniline containing chlorine, $C_{18}H_{14}Cl.N_3$, by means of a boiling solution of chloride of lime. Leichti has mentioned the fact that working on a large scale, in 1876 he transformed ordinary aniline black into ungreenable black. This was done by boiling with dilute chloride of lime, and he states that by this method he obtained better results than with chromic acid.

The blacks obtained on the fibre by dyeing or printing usually turn green under the action of acid, and of sulphuric acid in particular. The purer the aniline used the more likely this is to occur. The black obtained with heavy aniline, which contains ortho- and para-toluidine and even xyloidine, is much less greenable. The complaints of dyers and printers of the greening of the black increase in proportion to the purity of the aniline delivered to them. The remedy, therefore, would seem to be simple, and to consist merely in using impure aniline. Unfortunately, however, the black obtained with this is not so fine as that got with pure aniline.

The theory of this greening is simple. As we have seen, aniline gives various oxidation products by the action of acid oxidants. The first of these, emeraldine, is an indigo blue in its basic state, whereas its salts are a bright green; the second, migraniline, or aniline black, is a dark violet in the basic state, and its salts are dark green. By the action of sulphuric acid, nigraniline is probably reduced to the state of emeraldine.

Bichromate of potash transforms nigraniline into a chromate, which Nietzki has analysed. This is not turned green by non-reducing acids, but on the other hand, greens under the action of sulphurous acid by reason of the reducing properties of this acid. Chromic acid, acid ferric salts, chlorates in the presence of salts of copper and sal ammoniac, acid chromate, the hypochlorites and many other oxidants transform ordinary aniline black into the black which has been conventionally termed ungreenable black. This black is not sensibly greened by acids or by sulphurous acid gas. A black absolutely insensible to the action of sulphurous acid and to the influences of the atmosphere, does not appear to exist; the blacks which are only slightly altered may be considered in practice as sufficiently ungreenable.

All the blacks, whatever may be the method of formation, can be rendered ungreenable by the action of oxidants. This has been pointed out by Lauth, who, as a supplement to his patent (*E.P.* 1421-1869) relating to the production of aniline black over

manganese bistre makes the following remark on the importance of a post oxidation of aniline black (*M.S.* 1873, p. 794).

"After dyeing it is possible with the aid of certain agents to modify the shade or increase its intensity. This fact seemed to me to be curious; it seemed to indicate that at the moment the dioxide of manganese had terminated its action, the colouring matter thus produced, possessing all the properties of the black, is nevertheless still in an intermediate state, and that ulterior oxidation is useful to bring it to a definite state.

"Bichromate of potash, 1 gramme per litre, the salts of copper, chromium or mercury, and especially a mixture of one gramme per litre each of chlorate of potash, a copper salt and sal ammoniac, greatly increase the intensity of the black. The goods should be treated with the chosen oxidant after the washing which follows dyeing, and kept in the liquor for half an hour at the boil, then lifted, washed with water, and soaped hot.

"This process gives very fine and absolutely fast blacks. It does not tender the fibre and it is quick. As a set-off to these advantages, however, there are certain disadvantages which I have already noted with respect to mordanting and another which I have not yet mentioned, and this is, that the black always rubs a little. I note here a few of the styles obtainable by my process:

1. Self blacks.
2. Black bottoms, with discharge effects in all colours.
3. Grey, by the use of weaker mordants than for black.
4. Black prints, by the side of grey and all other shades capable of resisting the operations already indicated. (Iron, chromium, copper, indigo, cutch, etc.)
5. Styles obtained by the simultaneous action of indigo and of the black, a blue bottom with white discharge printed over with black. The nature of the alkaloid used in the dye-bath is of first importance for the success of the black, pure aniline alone gives a very fine and very intense black.

Toluidine gives a bluish grey, methylaniline a violet black, and naphthylamine a violet brown.

"The differences of shade produced by aniline and toluidine are great enough to recommend this process as a method of judging the comparative values of commercial aniline. For this purpose cloth prepared as for testing madder is used, and the aniline to be tested is dyed in comparison with dyeings got with known products."

Brandt (*B.S.M.* 1876, p. 441) topped aniline black with aniline violet in order to make the black ungreenable. The violet absorbed by the black resists a very energetic chlorination, and this proves that the result is more than a simple effect of light, and confirms the affinity of developed aniline black for the basic colours.

Jeanmaire, at the beginning of 1876, suggested a process of treating aniline black in order to make it ungreenable. This process was used regularly by the firm of Koechlin Frères, commencing in April, 1876, and was described in a sealed communication deposited with the Société Industrielle de Mulhouse. This was opened and published at the request of the firm, in consequence of a personal difference with S. Grawitz. The process is still used, and is as follows:—

Under the influence of acid reducing agents such as sulphurous acid, or sulphuretted hydrogen in solution or in a gaseous state, aniline black takes a greenish colour, arising from its transformation more or less into emeraldine. The emeraldine, which in an alkaline state is dark blue, becomes green under even the mildest treatment with acid.

There is a body in a state of oxidation superior to that of ordinary aniline black, which is not transformed into emeraldine by the action of alkaline or acid reducing agents. This body is obtained as follows:—

The dyed or printed aniline black is passed through a bath, in which it is submitted to the action of an acid oxidant at a temperature of at least 75° C. All that remains to be done is to soap the goods, or even simply to rinse them.

There is a choice of a large number of oxidants for this purpose; the best are the ferric salts, chromic acid, and easily decomposed chlorates such as chlorate of aluminium. The solution of the ferric salt is prepared by adding to a ferrous salt, once or once and a half its weight of sulphuric acid at 66° B. This avoids the deposit of oxide on the cloth. The ferric salts are less easy to procure than the ferrous salts; sulphate of iron produced by the action of crude sulphuric acid or iron pyrites is on the market at a very low price, and this is used in preparing the ferric solution. Dissolve 20 kilos. of sulphate of iron in 60 to 70 litres of water, add 5 kilos. of bichromate of potash, and 15 to 18 litres of sulphuric acid at 66° B. The quantity of water indicated is absolutely indispensable, as the heat produced by the mingling of the acid and water is necessary to dissolve the acid ferric sulphate, which is otherwise soluble with difficulty. Six to eight pieces are worked in a madder vat at a time, using one to two litres of the solution. They are treated at 80° C. for half an hour to an hour.

For the black and orange style chromic acid is preferably used, to the extent of 300 to 400 grammes for six to eight pieces, that is to say, 300 to 400 grammes of bichromate and a quarter of a litre of sulphuric acid. The goods are worked as with the ferric salt, and it then remains to develop the orange in alkaline chromate. For the black and fast blue (indigo) style it is indispensable to leave a slight excess of ferrous salt in the bath as the chromic acid destroys the blue. Four kilos. of bichromate are used instead of five, as given in the recipe above.

Ungreenable black can also be obtained by the processes of

Bobœuf, Paraf-Javal, Persoz and others, commencing in the cold bath and raising the temperature or by steaming the black before washing.

A. Kertesz (*C.Z.* 1890, p. 12) says that ungreenable steam aniline black cannot be obtained except in the absence of free mineral acid. The old theory, according to which ungreenable black is not produced except by super oxidation, should therefore be completed; the action of alkaline ferrocyanides in the generation of ungreenable steam aniline black is explained by the fact that they neutralise the mineral acids, producing ferrocyanide of aniline. When the oxidation is produced under these conditions in the absence of free mineral acids, ungreenable black is formed. It is probable that the alkaline ferrocyanide gives an ungreenable black simply because the Prussian blue, produced on steaming, combines with the aniline black. Kertesz does not decide this question.

As a demonstration of his views, Kertesz states the results of various experiments. A cotton fent is padded with ordinary vanadium black, dried and steamed. The black obtained turns green. If to the same bath ferrocyanide of ammonium is added, and the bath is brought to the same concentration, a fent padded in this and then dried and steamed takes an ungreenable black. If to this mixture an excess of hydrochloric acid is added without modifying the concentration of the bath, a greening black is obtained anew. The bath for the ordinary aged aniline black is made as follows: 2,600 grammes of aniline oil are mixed with 2,900 grammes of hydrochloric acid at 19° B., and to this is added 1,500 grammes of chlorate of soda dissolved in just sufficient water, and 300 grammes of aniline oil. This bath is brought up to 31½ litres, and 66 cc. of vanadic solution is added. The quantity of hydrochloric acid can be reduced to 2,500 grammes without the intensity of the black suffering, but with 1,800 grammes of hydrochloric acid a dull black is produced. A fent is padded in the bath made in this manner and steamed in the Mather and Platt; the result is a black, which turns green. Even prepared with chlorate and tartrate of aniline it turns green after steaming. The strongly recommended addition of tartaric acid to steam aniline black, under pretext that it aids the formation of chlorate of aniline, is useless, according to Kertesz, as chlorate of aniline by itself has no influence on the production of ungreenable black. If the chlorate of soda in the recipe above is replaced by a corresponding quantity of chlorate of ammonium, the black still turns green. Kertesz obtained a very fine ungreenable black following the same process, but adding about 8 litres of ferrocyanide of ammonium solution. This is prepared by dissolving 18 kilos. of ferrocyanide of potassium in 32 litres of water, and adding to it 9 kilos. of sulphate of ammonia dissolved in 13 litres of water. The sulphate of potassium is allowed to crystallise out of this mixture, and the clear supernatant liquor is used, one litre of which corresponds with 340 grammes of ferrocyanide of potassium.

By adding to this mixture the necessary proportion of thickening, an excellent printing colour is obtained, which gives a completely ungreenable black, capable of being steamed for a long time without tendering the fibre. Experiments made with equivalent quantities of alkaline ferricyanide have given analagous results. The shade seems even fuller, and probably may be improved by slightly increasing the proportion of the oxidant.

The superiority of the prussiate aniline black over all others is due to the fact that the hydrochloric acid can be completely neutralised, as in this particular case the presence of free acid is not necessary to the formation of the black.

Prud'homme (*B.S.M.* 1890, p. 55 and p. 220) recommends a mixture of aniline with toluidine and xylydine for the production of ungreenable black. A mixture of equal parts of ortho- and of para-toluidine should give an excellent black, ungreenable without super-oxidation. D'Andiran and Wegelin have been granted a patent (*E.P.* 4,123, 1879) for this process, which they purchased from the inventor. The preliminary mixture of alpha- and betanaphthylamine, and more particularly of paraphenylenediamine with aniline has been patented by C. Monnet (*D.R.P.* 37,661, 1886).

A. Scheurer (*B.S.M.* 1890, p. 129) has increased this list by the addition of toluidine, benzidine and dianisidine, after Binder had found that benzidine oxidised under the same conditions as aniline gives a brown, and that Scheurer himself had observed that dianisidine gives a bistre.

Dreher (*D.R.P.* 127,361) patents the addition of metanitriline. This base when oxidised alone, gives also a brown. Dreher's bath for oxidation aniline black contains, per litre, 60 grammes of aniline oil, 60 grammes of beta nitriline, 160 grammes of concentrated hydrochloric acid, 60 grammes of chlorate of soda, 25 grammes of sal ammoniac, and 20 grammes of nitrate of copper. Schmid (*C.Z.* 1892, p. 245) argues that the proportion of hydrochloric acid and chlorate of soda is too large, and will tender the fibre, and at the same time the addition of metanitriline will largely increase the cost of dyeing.

E. Grandmougin (*Z.F.* 1906, p. 141) mentions that the addition of 10 per cent. of hydrochloride of paraminophenol to the aniline salt gives a black still less liable to turn green, and that this is more economical than the addition of nitriline. The same chemist (*Z.F.* 1906, p. 286) among other processes, shows that by padding a black, either a self colour or topped with a solution of chlorate of aluminium, finishing by adding a little ferricyanide and steaming, an excellent result is obtained.

Oehler's Aniline Salt gives a fine full black, absolutely ungreenable. The inventor, F. V. Kallab, recommends that it should be used in the ordinary manner, and developed preferably in the Mather and Platt. This salt is the hydrochloride of a commercial metatoluidine containing a certain quantity of isomers, ortho and

para. It is obtained by the reduction of commercial metanitrotoluene, separated by fractional distillation from the major part of its isomers. A printing paste can be prepared, for instance, with 100 grammes of Oehler's Aniline Salt, 30 grammes of chlorate of soda, and 50 grammes of sulphide of copper paste per kilo of colour. The black obtained is ungreenable without after treatment. Practically a very resistant black is got by mixing one part of Aniline Salt and 4 parts of ordinary aniline salt.

A. Scheurer (*B.S.M.* 1900, p. 128) states that Jeannolle's black, which is prepared by means of salts of iron, and consequently contains iron, can be rendered ungreenable by after-treatment in a hot bath of dinitrosoresorcin. Scheurer (*B.S.M.* 1902, p. 132) also describes a process used at Thann, which has given excellent results in preparing ungreenable black. This consists in adding a small quantity of aniline salt to the super-oxidation bath at a high temperature described by Jeanmaire. The bath contains per litre 10 grammes of aniline salt, 10 grammes of cupric chloride, and 5 grammes of chlorate of potash. The developed, chromed and dried pieces are padded in this bath, then steamed for two minutes at 100° C.

F. Weber (*B.S.M.* May, 1900) recommends the treatment of the finished pieces with aniline salts and chlorates. Grossheintz (*B.S.M.* June, 1900) obtains good results with a bath containing per litre of water, 6 grammes of aniline oil, 6 grammes of hydrochloric acid, and 5 grammes of chlorate of soda. The strength of the acid is not stated, but it probably is 18° B. The material after the final development of the black, is passed through this bath, dried, steamed for four minutes, then washed and soaped. The black obtained is very fast to light, but the process can only be used for self colours, as the bath tints any white in the pattern.

Mura (*B.S.M.* March and June, 1900) uses bichromate of soda in the presence of aniline salt. Treatment with bichromate alone does not render the black ungreenable. According to his instructions the goods are either padded through a bath containing 10 grammes of bichromate of soda and 2 grammes of aniline salt per litre, then dried and steamed for three minutes, or the developed and chromed black is worked in the same bath for twenty minutes at the boil. Schmid remarks that Mura's process prevents the black from turning green, but dulls it considerably. Scheurer's process is preferable, as the results are much better. Chlorate of copper alone, if the treatment is sufficiently prolonged, renders the black ungreenable, but its action is much more rapid in the presence of aniline salt. Meister, Lucius and Bruning recommend chlorate of aluminium for the same purpose.

Printed aniline black, to which Scheurer's process cannot be applied, is rendered ungreenable if acetate of lead is added to the finish. As we have already seen heavy anilines, which in addition to aniline contain toluidine and xyloidine, give a black that is not very liable to turn green. This arises from the fact that

metaxylidine and paratoluidine oxidise to browns, which mask the green colour.

Finally, we give two recipes contained in sealed documents deposited with the Société Industrielle de Mulhouse, and opened in July, 1907:—

Jeanmaire, October 29, 1896: After fixing the colour and scouring without soap, pad with a mixture of chlorate of potash, sulphate of alumina and red prussiate. Steam according to circumstances for a quarter to half an hour and wash, or use chromate of ammonia in the same way. Scouring must be done without soap, as this is very difficult to rinse out, and any residue destroys part of the fixing bath, and is likely to cause stains and unlevel colour.

F. Oswald, March 2, 1897: Pad in alkaline chlorate with an addition of a trace of chloride of vanadium, and dry at 75° C. This mixture could be added to the finish.

CHAPTER IV.—Textile Printing with Aniline Black.

ALBUMEN PRINTING.

Aniline black, obtained in the preparation of Perkin's Mauve, as we have already noted, was used in textile printing. To begin with, the black was simply a by-product, but soon colour makers commenced to prepare it independently. The method of preparation was described first by Bobœuf and Alland, then in 1866 by Dullo. It was put on the market about 1870 by Heyl Bros., of Charlottenburg. Armand Muller described a process of obtaining it, and Glanzmann produced ungreenable black pigment with the aid of bichromate of potash.

Florian Ganzer, a chemist with the firm of Dollfus, Mieg and Co., prepared aniline black in paste for albumen printing in October, 1868. He added a mixture of aniline and chlorate of potash gradually to sulphuric acid of medium strength. When the reaction had ceased, he washed the black mass obtained with a large quantity of boiling water, and got in this way a very fine black, which made an excellent printing colour. Gustav Engel, who gives us this information verbally, about the same time prepared a black in paste by heating two parts of aniline and one part of picric acid crystals for five hours in a bath of paraffin at 140 to 160° C. The operation was finished when a drop of the mixture took the form of a solid mass on cooling. The mixture was then run on a slab, allowed to cool, and pulverised. The coarse powder obtained was washed, to begin with, with dilute hydrochloric acid, then with weak ammonia, and finally with pure water, and dissolved in the least possible quantity of concentrated sulphuric acid. An abundant addition of cold water precipitates the black from this solution, giving a very fine black in paste, specially suitable for pigment printing.

Kruis (*M.S.* 1874, p. 927) obtained the black by the action of a salt of a heavy metal on a mixture of chlorate of potash and of aniline salt.

Glanzmann (*B.S.R.* 1874, p.121) gives the following process:—One litre of water and 100 grammes of hydrochloride of aniline are boiled, a solution of 30 grammes of sulphate of copper in 600 cc. of water is poured slowly in, and after heating up again a solution of 52 grammes of bichromate of potash in 600 cc. of water is added gradually, boiled for three minutes and filtered.

Depierre in his book on dyeing recommends the following recipe: Dissolve 1 kilo. of aniline salt in 10 litres of water, 350 grammes of hydrochloric acid, and 1 kilo. of sulphuric acid at 60 deg. B. in 3 litres of water, and 1 kilo. of bichromate of soda in 7 litres of water; mix these three solutions, boil for about two hours, and collect the precipitate by filtration.

PRODUCTION ON THE FIBRE.

As we have already noted, Runge was the first to suggest the formation of the oxidation products of aniline on the fibre itself. Wilm (*M.S.* 1861, p. 75) also made several experiments with the same aim. About this time also three English chemists, Calvert, Clift and Lowe, patented a commercial application of this reaction (*E.P.* 1426-1860). In describing this patent, the *Chemical News* remarked: "This curious patent may be divided into two principal parts, one being the production of a green colouring matter from aniline and its homologues, and the other being the conversion of the green colour into a blue. The green they call emeraldine, and the blue azurine. The chemists who devote themselves to colouring matters are said to be at their wits' end for names. The patentees do not appear to have succeeded in isolating their new colouring matters, for it is specially stated that they are obtained by oxidation in direct contact with the yarn, etc. In preparing the green colour, they first impregnate the goods with an oxidising agent. They recommend a solution of chlorate of potash (4 oz. to the gallon), the goods, after steeping, are to be dried and then padded or printed with an acid salt of the base. They prefer a solution of tartrate or hydrochlorate of aniline containing one per cent. of the alkaloid. After the padding or printing, the goods are aged for twelve hours, that time being sufficient for the complete development of the colour. They also prepare the green by the following modification of the first process:—They mix the oxidising agent with the salt of aniline, and print on both together, of course thickening with starch or flour in the usual manner. They recommend the following mixture:—‘Solution of an acid salt of aniline (containing 1 lb. of aniline)

Tartrate or chloride of aniline	3 lbs.
Starch or flour paste	60 „
Chlorate of potash	1 „

The chlorate of potash must be dissolved in the starch paste whilst hot, and the solution of the acid salt of aniline added to it after cooling.’ We quote the above literally because it appears to us rather vague. If we understand the directions, they mean that 3 lbs. of a solution of tartrate or ‘chloride’ of aniline are to be taken, which 3 lbs. of solution are to contain 1 lb. of aniline. The green colour as produced by the above method is to be converted into a blue or purple by boiling in a weak solution of soap or alkali, the goods are then to be dried. The soap solution should contain 4 oz. of printers’ soap to the gallon, and the alkaline bath one ounce

of caustic soda to the gallon. The patentees say that instead of the alkaline, or soap bath, the goods may be passed through a solution containing one ounce of chromate or bichromate of potash to the gallon of water. The above colours do not require any mordant. This patent appears to us to be of great interest. We know that efforts have, for a long time past, been made to apply aniline directly to fabrics, and convert it into colouring matter in the fibre. Some of these efforts have led to disappointment. If yarn impregnated with a salt of aniline be passed into a solution of a chromate or bichromate, it immediately assumes a dirty green colour, which acquires a certain amount of purple tone by treatment with soap. If the aniline solution be strong, the goods become nearly black in the chromate bath."

E. Kopp (*B.S.C.P.*, 1860, p. 204) made experiments on the formation of aniline black on the fibre, and on the properties of the black thus obtained. He printed nitrate of aniline with chlorate of soda, and found that the black drew towards a blue on treatment with alkalis, and to a green with acids. He proved also that aniline black could be produced by ageing or steaming a fent printed with nitrate of aniline and red prussiate.

In his "Lectures on the Coal Tar Colours," p. 63, which appeared in 1863, Crace Calvert makes the following remarks:—"Although it has long been known to chemists that aniline would yield a green colour when submitted to the action of certain oxidising agents, up to the present time all efforts to dye silk and wool with it commercially have failed, but in 1860, Messrs. Calvert, Clift and Lowe introduced a most easy and practical method of producing it, under the name of emeraldine, on cotton fabrics, specimens of which were exhibited in the Chemical Department (of the Exhibition of 1862). The process consists of printing an acid chloride of aniline on a cotton fabric prepared with chlorate of potash, and in a few hours a beautiful bright green gradually appears, which only requires to be washed. If the green fabric is passed through a solution of bichromate of potash this colour is transformed into a dark indigo blue, called azurine. The production of this colour directly on the fabric is most important, and it will probably lead to the similar production of the other coal-tar colours, without previous treatment, directly on the cloth. By this means not only the great loss of aniline in the original production of the colour will be avoided, but a considerable economy of mordants will be effected. These chemists also induced Messrs. Wood and Wright at the end of 1860 to produce by their process dark green or blue, which they considered sufficiently good to be introduced into the market, and Messrs. Wood and Wright have further effected an improvement in these dark shades, which may be called black, by adding to the chlorate of potash per-salts of iron or other oxidising agents; also by oxidising the colour thus produced on the fabric (which is the chief novelty of this process), either by a weak solution of bichromate of potash or bleaching powder. Nitrate of copper may

be mixed with the hydro-chlorate of aniline, without the addition of chlorate of potash, and the mixture printed on the fabric, when gradually a dark green or black is produced. This mode of printing directly on the fabric gives green or blue, so dark as to be almost identical with black."

In Crace Calvert's work there is a specimen pattern of emeraldine which shows a dark green, and a sample printed by Wood and Wright which is a full black.

J. Lightfoot, of Accrington (*E.P.*, 151, 1863), perfected the process of producing aniline black to such a degree that he may be considered as the veritable inventor. Calvert, Clift, and Lowe's printing colour contained very acid hydrochloride of aniline, and this attacked the copper printing rollers; the black then developed better and more rapidly than when it was printed with wooden blocks. Doubtless Lightfoot noted this, and the fact led him to add copper to the colour itself. He describes his process as follows:—"I take one litre of water and dissolve in it 25 grammes of chloride of potash; I pour into this aniline or an analogous compound, but preferably aniline, in the proportion of 50 grammes, and an equal quantity of hydrochloric acid. When these solutions are thoroughly mixed I add 126 c.c. of acetic acid, and 50 grammes of chloride of copper, Sp. G. 1.44, then 25 grammes of sal ammoniac or an equivalent quantity of an alkaline chloride. After having steeped the yarn or cloth in this solution I squeeze it and dry. I allow it to rest for two days, then pass it through a weak bath of soap or soda, or better still, through a weak solution of chloride of lime. By this series of treatments I obtained an intense black."

For a printing colour the water is replaced by an equal quantity of starch thickening. The beauty, fastness and cheapness of this black proved the importance of Lightfoot's discovery, and accounted for the general haste to make use of it. Unfortunately, the process as it was first described, was by no means without its faults. The inventor himself, who had pointed out a long series of metals capable of replacing the copper, was obliged to modify it. To begin with, the chloride of copper contained in the printing paste attacked the doctors, with the usual result of scratches on the printed cloth, and the acid damaged the rollers. Moreover, the printing paste became changed in composition, even at the ordinary temperature, with the result that the aniline commenced to oxidise before printing, and a sufficiently intense black was not obtained. Finally, the cloth itself was very often tendered by the acid or the acid salts contained in the colour.

Kopp (*M.S.*, 1863, p. 531) sought to remedy these faults in the following manner. The cloth was first padded in a weak solution of chlorate of soda, 3 to 4 grammes per litre, and to this was added a determined proportion of arsenite of soda, in quantity rather more than that of the chlorate as a rule. The cloth was then dried and printed with the aniline colour, containing per

litre about 70 grammes of hydrochloride of aniline, half this weight of chlorate of potash, and ferrous chloride, and the necessary thickening. The copper was thus superseded. The ferrous chloride changes by oxidation into basic ferric chloride. It nevertheless has an acid character, and is capable of decomposing the chlorate, thus playing the part of the chloride of copper in the older process. The printed cloth is treated in the same manner. It is less tendered, and the process permits several compound styles to be produced, as, for instance, the black and madder violet style.

Camille Koechlin modified Lightfoot's process by treating the cloth to begin with with a salt of copper, and then printing on a mixture of chlorate of potash and hydrochloride of aniline. This method is troublesome, and moreover, there are few colours that can be fixed under these conditions by the side of the aniline black. In an article signed "Omega," in the *Moniteur Scientifique* of 1864, p. 433, it is mentioned that attempts had been made to replace the copper salt by bichromate of potash, in treating the cloth before printing.

Cordillot (*E.P.*, 3045-1863) proposed to replace the copper salt of Lightfoot's process by a ferricyanide, preferably ferricyanide of ammonium, either alone or with chlorate of potash, tartaric acid, or hydrochloride of aniline. In many respects this process was superior to the preceding one, but it also had its weak points. It was expensive, and the printing colour was not stable. Nevertheless, it has the great advantage that it gives a fine, remarkably fast black, which becomes ungreenable on steaming.

For steam black the hydrochloride of aniline is replaced by the tartrate; later the ferricyanide of ammonium, which is very expensive, was replaced by the potassium salt; and finally by increasing the proportion of chlorate, preferably the chlorate of soda or of barium, ferrocyanide of potassium could be used instead of ferricyanide. With these modifications Cordillot's process is still used on a large scale, especially for steam black developed in the Mather and Platt, a process which we shall describe more fully later.

Cordillot was colourist with the firm of Huguenin Schwartz and Conilleau at the famous Mer Rouge Works near Mulhouse, Alsace. Schlumberger (*B.S.M.*, June, 1889) described several of his experiments to A. Scheurer in a letter dated May 28th, 1889. We give the principal passages: "The first experiments that Cordillot made at the Mer Rouge on the production of aniline black date, according to our laboratory book, from April 22nd, 1863. He tried a printing colour containing ferric chloride, chloride of chromium, chlorate of potash, sal ammoniac, and aniline salt. The following year he tried a sulphate of iron black, then nitrate of iron and tartrate of iron. On January 16th, 1864, the ferricyanide black was discovered; this was soon used on a large scale."

A private communication from Cordillot shows that the first

successful experiment with ferricyanide of ammonium had been completed in October, 1863. Huguerin-Schwartz and Conilleau sold the process to Muller Pack, of Basle, after experiments directed by Albert Schlumberger had shown that the new process allowed 40 pieces to be printed without the necessity of re-setting the doctors, and that the black developed by moist heat in the oxidation chamber resisted boiling soap, was perfect after finishing, and did not tender the cloth. During the negotiations with Muller Pack the process was kept scrupulously secret, and this explains why the first mention of it in the laboratory book was not made until January 16th, 1864.

Charles Lauth (*E.P.*, 1409, 1864) must be credited with the most important improvement of Lightfoot's aniline black. His process is still in regular use. After a large number of experiments Lauth recognised that the presence of a copper salt, or of a metal of which the chlorate is easily decomposed, is indispensable for the production of the black. In the course of his research he found it was impossible advantageously to use soluble metallic salts, and in particular the salts of copper, and he therefore turned to an insoluble copper compound, inactive during the printing process, but capable of eventually becoming soluble and active. Sulphide of copper fulfilled these conditions. In the oxidation chamber it is transformed into sulphate by the chlorate, and is then in the condition exacted by Lightfoot's process.

Lauth gives the following directions: For 10 litres of starch thickening take 350 grammes of chlorate of potash, 300 grammes of sulphide of copper in paste, 300 grammes of sal ammoniac, and 800 grammes of hydrochloride of aniline. The printed cloth is passed into the oxidation chamber, and after development washed with pure or alkaline water. Lauth's method greatly increased the profitable utility of Lightfoot's discovery.

Camille Koechlin crowned the edifice which was the work of so many hands. He replaced the hydrochloride of aniline by the tartrate. This does not attack even the most delicate tissues, and moreover, has the advantage over the hydrochloride of having no effect upon the mordants that may have to be printed at the same time. The tartrate alone is not capable of giving a black, but in the presence of hydrochloride of ammonia, a slow double decomposition is produced on the fibre with the formation of hydrochloride of aniline. The proportion of hydrochloride of ammonia in the printing paste is increased for this purpose. The after treatment of the goods is the same as for Lauth's black.

Camille Koechlin also recommends the use of a basic salt of aniline instead of the tartrate, which is expensive. The basic salt is prepared by adding to aniline neutralised by hydrochloric acid, an equal quantity of the free base. The more acid the aniline salt, the more rapid is the development of the colour, but the acidity tenders the fibre. On the other hand if a basic salt is used, or even aniline alone, the black does not form at all.

It is necessary therefore in practice to hit upon a happy medium.

Alfred Paraf (*E.P.*, 804, 1865) recommends that the hydrochloride of aniline should be dissolved in hydrofluosilicic acid at 8°B, thickened, and printed on cloth prepared with chlorate of potash, and developed by ageing at 32 to 35° C. When the colours printed together with the black allow it, the chlorate may be added directly to the colour paste. This black contains no metal, and Paraf affirms that it is ungreenable. Nevertheless it develops only when it is printed with copper rollers, which introduce this metal into the colour. Rosenstiehl notes that pure non-acid hydrochloride of aniline does not give the black at the temperature of the oxidation chambers, but that this is produced by the least trace of copper. We have noted this fact already in writing the theory of the formation of aniline black.

J. Higgin (*E.P.* 897-1866) recommends the precipitation on the fibre of an insoluble chromate, which will contribute to render the black ungreenable. The complete specification also protects the use of tungstate of chromium mixed with the chlorate and aniline salt. Kielmeyer (*Entwicklung des Anilinschwarz*, 1893) says that this black does not bleed into other colours either on ageing or steaming, and keeps the outlines of the patterns clear and sharp. There is the disadvantage, however, that the tungstic acid is reduced to oxide of tungsten, and this is changed by the action of the hydrochloride of aniline into red chloride of tungsten, which deposits on the steel doctors with the usual troublesome consequences.

Alfred Paraf (*B.F.*, 71692-1866) produces an aniline black by printing a colour thickened with starch and containing 34 grammes of hydrochloride or other salt of aniline, 500 grammes of chlorate of chromium in paste and chlorate of potash. The colour is developed by ageing. This black will stand steaming. To accelerate the oxidation when necessary 2 to 3 per cent. of hydrofluosilicic acid or arsenious acid may be added to the printing paste. To avoid the alteration of the colour by the chromic acid which gradually returns to a free state, a small quantity of a substance capable of combining with the chromic acid and of forming an insoluble compound with it is added, barium chloride, for instance. If the author recommends to begin with the use of chromate of chrome, it is because of the advantage of oxidising with the chromic acid at a single operation, instead of resorting to the usual after-chroming. By using totally or partially insoluble salts of chromium the chromic acid is set at liberty on ageing or steaming. The chromates of iron, the basic chromate of lead, and other more soluble salts, such as the bichromate of chromium and of manganese and the chromate of manganese may be used in this way.

F. Witz (*B.S.M.*, December, 1892) gives the following recipe for the chromate of chrome black:—Boil together 60 litres of water, 8 kilos. of white starch, 6 kilos. of British gum, $\frac{1}{2}$ kilo. of aniline, and 4 kilos. 300 grammes of chlorate of soda; add when cold 9 kilos. of aniline salt, and immediately before use add per 10 litres

of colour, 250 grammes of sal ammoniac and 150 grammes of chromate of chrome. This same process depending upon the employment of chromate of chrome was tried later (in 1881) in England by Joseph Schmidlin, and is still used. To prepare the chromate of chrome Witz made a boiling solution of 12 kilos. 586 grammes of chrome alum in 70 litres of water, and a boiling solution of 13 kilos. 713 grammes of chromate of potash in 70 litres of water. The precipitate is washed thoroughly and gives 33 kilos. of paste.

J. Higgin, in a second patent (*E.P.*, 2351-1868), tried to prepare hydrochloride of aniline containing no excess of acid, and to make up the colour paste by adding chlorate of potash and a salt of copper to this salt. In order to do this he mixed aniline with the chloride of a metallic base, which does not hinder the formation of aniline black. Used in proper proportions the precipitation of the metal can be wholly or largely avoided, and a soluble hydrochloride finally obtained which contains chlorine combined with "metalaniline." The chlorides of iron and of chrome are preferably employed. Although Higgin's method is correct in itself, his interpretation is erroneous, as we have already seen. In the same patent he protects the substitution of the sulphocyanide of copper for the sulphide. This compound is used in England under the name of "white paste."

Lauber gives the following process for a colour paste made with sulphocyanide of copper:—Boil together 6 kilos. of starch, $1\frac{1}{2}$ kilos. of light British gum, 48 litres of water, 6 litres of gum tragacanth water (62 grammes per litre), and add while hot 2 kilos. chlorate of potash and $1\frac{1}{2}$ kilos. of sal ammoniac, then allow to cool, and add 12 kilos. of aniline salt, 5 to 8 litres of aniline, and 1,875 grammes of sulphocyanide of copper. Lauber states that this black oxidises more slowly than the black obtained with sulphide of copper, but has the advantage over it of requiring less care in printing and oxidation. The proportion of chlorate of potash in the recipe above is certainly too small.

A. Spirk gives the preference to the following colour for block printing:—Dissolve 30 grammes of acetate of copper, 30 grammes of chlorate of potash, and 75 grammes of hydrochloride or nitrate of aniline in 2,600 grammes of starch paste still hot. The colour develops after ageing for 8 to 12 hours and is transformed into a full black by a passage through soda. Spirk also gives several recipes for roller printing pastes, employing sulphate of copper and hydrochloride or tartrate of aniline, and, in addition, describes a tungstate of chrome black made by boiling 2 litres of water, 270 grammes of wheat starch, and 375 grammes of tungstate of chrome in paste, and when lukewarm, adding 60 grammes of chlorate of potash and 30 grammes sal ammoniac and, after cooling, 210 grammes hydrochloride of aniline. The tungstate is obtained by double decomposition between chloride of chromium and tungstate of ammonium.

Lauth's French patent (85554-1869) specially points out the manner of dyeing and fixing a black developed by no matter what method. The specification also describes a printing process in which a neutral salt of aniline is employed, and precipitated peroxide of manganese and sal ammoniac or any other substance capable of decomposing the peroxide of manganese on steaming. This black is steamed after printing. The peroxide of manganese can be replaced by other metallic oxides or acids rich in oxygen.

The experience of colourists having shown that aniline salt, in the absence of metal, does not give the black at the temperature of the oxidation chambers when wooden printing blocks are used, but on the other hand, gives it readily when a trace of copper is added, Lightfoot endeavoured to ascertain if other metals exercised an analogous action. He printed with a hand block a colour containing basic hydrochloride of aniline and chlorate of ammonia thickened with starch, and pressed thin plates of the metals to be tested over the printed cloth for 15 minutes. The cloth was then exposed to a humid heat for 12 hours and passed through an alkaline bath. He found that vanadium developed the colour most rapidly, then copper, then uranium, and finally iron. The other metals seemed to have only a very feeble influence on the development of the colour. This shows the value of the salts of vanadium in aniline black printing, and the employment of them has become general since they have become cheap enough to compete with the salts of copper.

Kruis (*M.S.*, 1874, p. 927) studied the action of various salts of the heavy metals on the cold or hot solution of hydrochloride of aniline. He found that they all gave more or less rapidly a dark green precipitate, which turned grey or black in the air. Few of these salts, however, develop the black when they are printed with hydrochloride and aged. In addition to copper Kruis got good results with iron, manganese and cerium. He did not try vanadium. The finest black, in his opinion, was obtained with bisulphate of cerium. It was deeper, brighter and purer than the black obtained with the salts of copper. The manganese black was similar to that obtained with copper, the iron black inferior.

O. N. Witt (*C.I.*, 1896, p. 156) showed by experiment that the pure salts of cerium are without value for the production of the black. The results obtained by Kruis may be attributed to the presence of another metal in the salts of cerium which he employed.

We need merely mention the French patent 105,130 of Grawitz, according to which aniline should develop without acid on ageing, and the certificate of addition of only three days later in which the black is developed in the presence of acids. These patents are either a repetition of the work of Lightfoot and of Higgin, or a hotch-potch of practically unrealisable processes.

Wehrlin modified Cordillot's steam black in so far that instead of ferricyanide of ammonium in the printing colour he used the ferro and ferricyanides of aniline. These compounds are

prepared directly by the union of the base and the corresponding acids. He describes (*B.S.M.*, 1874, p. 386) the preparation of ferrocyanide of aniline. A solution of tartaric acid is poured into a solution of ferrocyanide of potassium. After filtering to separate out the tartar the liquid marks 38° B. A calculated quantity of aniline oil is dissolved in this at about 50° C. and allowed to crystallise. For the printing colour, this "ferrocyananiline" is thickened with white starch or British gum and sal ammoniac and chlorate of potash are added; or hydrochloride of aniline is added to the thickened ferrocyananiline. The exact recipe is not given. Ferricyaniline is made after the same fashion, but the printing paste prepared with it is more easily decomposed.

Ernest Schlumberger (*B.S.M.*, 1874, p. 390) prepares ferrocyananiline as follows:—Mix 2 kilos. of aniline oil and 2 kilos. of hydrochloric acid at 19° B. and allow to cool. Separately dissolve 2,400 grammes of yellow prussiate in 4,200 grammes of boiling water, allow to cool to 56° C. and add the hydrochloride of aniline. The ferrocyananiline crystallises out on cooling. The moist salt will keep for several days. Schlumberger expressed the opinion that it is more advantageous to use the ferrocyanide rather than the ferricyanide. All that is necessary is to increase the proportion of chlorate. For instance, 100 grammes of yellow prussiate requires 5 grammes of chlorate of potash to turn it into red prussiate.

Wehrlin, for a fine ferrocyananiline black without preliminary oxidation, recommends a simple steaming. Sal ammoniac and chlorate of potash are added to the solution of the salt thickened with wheat starch and light British gum. Proportionately diluted, the printing colour gives fine greys fast to soaping and chloping. A very intense black is obtained by mixing the ferrocyananiline with hydrochloride of aniline thickened with light British gum. The blacks obtained by this method do not turn green on exposure like the black got with sulphide of copper. The ferricyaniline under the same conditions as the ferrocyananiline gives a very fine black, even more intense.

Ernest Schlumberger also describes this method, and recommends ferrocyananiline prepared by the action of hydrochloride of aniline on yellow prussiate. He remarks that this salt has a great advantage over the ferricyanide. The printing paste obtained with the ferricyanide decomposes rapidly, and quickly becomes unsuitable for printing. That prepared with the ferrocyanide keeps an unlimited time, and moreover, does not attack the doctors, whereas the colour pastes prepared with ferricyanide have an injurious effect upon them.

Brandt is of the same opinion as Schlumberger. He remarks that Cordillot's black is not a steam colour, but is nevertheless the point of departure of all aniline blacks obtained with cyanide, and it can be changed to an excellent steam black when the proportions are modified. When

this black is to be developed by simple oxidation without steaming it is necessary to use a very acid colour and to oxidise at a high temperature. In spite of this it gives a black not sufficiently intense and too blue, a colour inferior in all respects to the sulphide of copper black which it was intended to replace. If, however, the attempt had been made to obtain a black by steaming instead of by ageing, the desired end would have been quickly achieved. As a matter of fact, a mixture of chlorate of aniline, hydrochloride of aniline, and ferricyanide of ammonium gives a very intense steam black, comparing favourably with any other except in the matter of price. The advantage as regards cost is on the side of Schlumberger's process.

In Albert Schlumberger's note above on the introduction of aniline black at the Mer Rouge Works, he showed that after Cordillot's ferrocyanide of ammonium black in 1862 a black had been prepared with chlorate of aniline, oxide of iron, and nitrate of copper, and in 1868 a nitrate of chrome black. Commencing in May, 1872, a black was used for some months containing only aniline salt and chlorate of soda; this was printed on cloth prepared with copper. A large number of pieces were also prepared with chromate before printing. Albert Schlumberger further remarks: "Finally, on May 7th, 1874, Frey, one of our chemists, experimented on the reaction of chlorate of iron, chlorate of copper, chlorate of chrome, and chlorate of aluminium on chlorate of aniline, and thus obtained precipitates, varying from a greenish black to a very intense yellowish black. The black obtained with chlorate of iron was recognised to be the finest. The black precipitates were submitted either dry or as moist pastes to sulphurous vapours and acids of all descriptions. They were treated successively with the most energetic acids. The precipitate obtained with chlorate of iron was in every case the most resistant and did not turn green. We therefore chose the iron black to print our mole-skirts. The definite recipe for the iron colour was formulated on June 2nd, 1874, and with improvements and modifications it has been used ever since. The precipitates have been the subject of many experiments since then, but a little of each of them still remains."

A. Guyard and Witz made interesting researches on the use of vanadium in the production of aniline black powder and on the fibre in dyeing and printing. Guyard calculated that one part of vanadium was amply sufficient to change a thousand parts of aniline salt into the black in the presence of the necessary quantity of chlorate of potash. Witz found that this transforming power of vanadium is enormous, and that a one hundred and thirty-five thousandth part or even a two hundred and seventy thousandth part is sufficient to oxidise the printing colour in a few days at 25° C.

In current practice .0012 of a gramme of vanadium per litre is used in a printing colour containing about 80 grammes of hydrochloride of aniline, and this corresponds to one sixty-six thousand

seven hundredth part of the weight of this salt. The quantity of vanadium to be employed varies in inverse proportion to the content in aniline, the temperature and the length of time taken in oxidation.

The hydrochloride of aniline is made slightly basic by the addition of $\frac{1}{2}$ to 1 c.c. of aniline, or of an equal quantity of ammonia per litre of printing colour. The relative proportions of hydrochloride of aniline and chlorate of potash are 1: 0.417. Lauth gives the proportion as 1: 0.437.

J. Schmidlin (*E.P.*, 3161-1879) recommends an aniline black for printing composed of aniline salt, chlorate of potash, insoluble chromate, and a salt of iron. As we have seen, Albert Paraf had patented in 1866 the employment of an insoluble chromate, and, in particular, of chromate of lead. In his German patent (*D.R.P.*, 13428), Schmidlin gives the following formula: 40 litres starch paste, 6 kilos. chromate of lead, 6 kilos. sal ammoniac, 6 kilos. aniline salt, and $1\frac{1}{2}$ kilos. chlorate of soda.

Sansone indicates the following proportions for Schmidlin's process: Boil 120 to 150 grammes of starch in 1,000 grammes of water, add warm, 200 grammes of aniline salt, and 200 grammes of sal ammoniac. Stir until the mixture is cool and add 50 grammes of chlorate of soda. Before printing add 200 grammes of chromate of lead (chrome yellow paste). Print on, steam for five minutes, wash and soap. Sansone states that even with only 100 grammes of aniline salt per kilo. of thickening this colour will still give a good black.

Glenk remarks that chlorate of barium, chlorate of soda, or even chloric acid in solution, is capable of replacing the more difficultly soluble chlorate of potash. Chlorate of barium is used with success in prussiate printing pastes, but it cannot be used in colours containing sulphates, as there is a precipitate of sulphate of barium which dulls the shade.

Goppelsroeder (*D.P.J.*, cc. xlv., p. 125) produced an aniline black on the fibre by electrolysis.

Thus the research of a multitude of colourists has made aniline black easy to produce. It has supplanted the majority of the blacks formerly in use, consisting either of a mixture of ultramarine and madder lake, iron and logwood lake, or iron-tannin lakes. Statistics published in 1892 by Albert Scheurer (*B.S.M.*, 1892, pp. 77 and 81) show that in Alsace alone 1,500,000 pieces were printed with Lauth's black from 1864 to 1892.

The superiority of Lauth's black caused its use to become general in the compound styles formerly in vogue. For instance, black along with chrome yellow or orange, or iron buff. Its greatest extension synchronises with the introduction of artificial alizarine in 1869. It does not require an iron mordant, and does not tinge colours printed at the same time; all compound styles with aniline black can be produced better and with less difficulty than by any method previously available.

CHAPTER V.—Printing Processes in Actual Use.

Among the numerous oxidation blacks which have been suggested, four only have been approved by practice, and these are actually in use. They are: 1, sulphide of copper black; 2, chromate of lead black; 3, vanadium black; 4, prussiate black.

Aniline is the base of all these printing colours; almost all its homologues yield blacks which are wanting in tone and in intensity. They are used, as we have seen, in mixture with aniline simply to prevent the black from turning green.

Recent researches of E. Ulrich and V. Fussgaenger show that an easily oxidisable base, paraminodiphenylamine, can be compared to aniline, and is even superior to it from certain points of view. We may therefore add to the four printing colours named the Diphenyl Black of Meister, Lucius and Bruning.

Aniline is used almost exclusively in the state of hydrochloride, which is known in practice as aniline salt. It is the cheapest of all the salts of aniline, and in comparison with the sulphate has the advantage of being much more soluble. Aniline oil and aniline salt are put on the market in a perfectly pure state. When aniline salt is prepared in the works, a solution of methyl violet, one gramme per litre, is used as indicator. This violet turns to green under the action of free acid. As we have already noted, a portion of the ordinary aniline salt, a quarter, or even more, may be replaced by an equal weight of Oehler's Aniline Salt.

Chlorate of soda is practically the only oxidant employed. Since it has been produced by electrolysis it has been put on the market in a very pure state, and it is more soluble and also cheaper than chlorate of potash, which was formerly used.

Sal ammoniac is almost always added to the printing paste. Its hygroscopic properties and the ease with which it splits up at a high temperature facilitate the reaction on the fibre during steaming.

1.—SULPHIDE OF COPPER BLACK.

As oxygen carrier insoluble sulphide of copper is mixed with the colour in the form of paste.

This is best prepared by precipitating a solution of flowers of sulphur in concentrated caustic soda lye with copper sulphate.

Copper Sulphide Paste.

Dissolve 500 grammes of sulphur in 3,500 grammes of caustic soda, 36° B., at 80° C. Then add a solution of 2,000 grammes

of copper sulphate in 8,000 grammes of water. Wash the precipitate by decantation and squeeze the water out of the precipitate until it weighs 2,500 grammes. This gives a 30 per cent paste.

Care must be taken to wash the sulphide of copper paste thus prepared very thoroughly, in order to remove completely all traces of sulphide of sodium or sulphate of copper in excess. The former will cover the printing rollers with a film of sulphide of copper, and this will produce faults in the pattern not easy to recognise at a glance. The sulphate of copper deposits the metal on the steel doctors, and these after a certain time damage the lines of the engraving. Sulphide of copper black, however carefully prepared, always attacks the copper rollers, but a simple polishing easily frees the roller from the fine film of sulphide formed on its surface. H. Schmid recommends the addition of 3 grammes of sulphocyanide of potassium per litre of printing colour to the paste, and the stability of the colour is considerably increased by this addition. Insoluble sulphocyanide of copper is probably formed by combination with the sulphate produced by the oxidation of the sulphide of copper.

Sulphide of copper black does not run either on ageing or steaming; it keeps the contours of the pattern clear and sharp, and gives an intense black which it is not necessary to chrome even in the case of heavy patterns. It is particularly suitable for printing shirtings, and is easily used together with steam colours or mordants.

It is best developed by slow oxidation, and this can be done in Preibisch's apparatus, or in the Mather and Platt for three minutes at a temperature not much above 65° C. It is still frequently developed by ageing. When it is printed together with steam colours it is necessary to submit it before steaming to the action of ammoniacal vapour.

As in spite of every care it prints less well than ferrocyanide blacks, and especially as the doctors have to be sharpened frequently, it is often replaced nowadays by prussiate black and this is always used when the iron which the prussiate contains will not harm the colours printed together with it, in the course of treatment after printing. The recipe for the sulphide of copper black is as follows:—

12 litres	water.
1,875 grammes	wheat starch,
750	„ dark British gum,
500	„ chlorate of soda.

Boil and add when cold

1,500 grammes	aniline salt,
90	„ aniline oil.

Immediately before use add

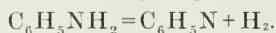
830 grammes sulphide of copper paste.

Another Recipe.

The sulphide of copper paste is prepared by dissolving 24 kilos. of sulphate of copper in 200 litres of water and adding with constant stirring $12\frac{1}{2}$ kilos. of sulphide of sodium dissolved in 50 litres of water. Filter through stretched calico, wash in hot water until all traces of sulphate of copper and of sulphide of sodium are eliminated.

Willstaetter's formula $(C_{12}H_9N_2)_x$, shows that three atoms of oxygen are required for two molecules of aniline, but in practice less is actually necessary, the oxygen of the air without doubt intervening. The black above contains 85.5 grammes of aniline salt, 5 grammes of aniline oil, and 28.5 grammes of chlorate per litre of printing colour. This corresponds to 92.5 grammes of aniline salt; to 100 grammes, therefore, there should be 30.8 grammes of chlorate of soda. A part of the aniline evaporates probably, and thus escapes oxidation. Moreover, the cupric salt also possibly contributes.

To establish a reasoned formula for aniline black printing colour, the method of transformation of the aniline into black must be taken into account, and this, as we have seen, is the result of the elimination of two atoms of hydrogen:—



To oxidise 100 parts of aniline salt, 37.5 parts of chlorate of potash, or 32.7 of chlorate of soda are necessary. It must be noted, however, that these relative proportions vary in different works.

The British gum, which is used as thickening, helps to prevent the tendering of the fibre by reason of its reducing properties.

Kallab recommends the following colour:—

70	parts thickening,
10	„ Oehler's Aniline Salt,
15	„ water,
5	„ sulphide of copper paste.

The thickening is prepared with

800	grammes	gum tragacanth water, 66 grammes per litre,
3,000	„	water,
720	„	wheat starch,
720	„	British gum,
220	„	chlorate of soda.

For heavy patterns Kallab recommends the addition to the printing paste of 50 to 60 grammes of ammonia per kilo. of aniline salt in order to set the aniline at liberty and to prevent the tendering of the fibre; it may be admitted that in the production of aniline black 19 grammes of hydrochloric acid gas are given off by each kilo. of aniline salt. Instead of the ammonia a certain quantity of yellow prussiate of potash may be added to the sulphide black. After development the goods are passed through a lukewarm bath of soda, washed thoroughly, then run in rope form through hypochlorite of soda, and finally soaped hot.

2.—CHROMATE OF LEAD BLACK.

The printing paste for this contains, in addition to an oxygen carrier, such as sulphide of copper, chromate of lead, which serves both as an oxidant and as a neutraliser.

This colour lends itself still better than the sulphide of copper black to the printing of fine designs, especially when it is printed together with colours which will not stand acid treatment, as the chromate of lead prevents the colour from running during development. Schmidlin invented the process, and we have already described it as modified by Sansone.

Its principal fault is that the developed black has a rather brown and dull tone. Its heavy content of solid matter makes it print rather badly. The cloth may be steamed for fifteen minutes without danger to the fibre. The following recipe is used in practice:—

1,750 grammes wheat starch,
 750 ,, dark British gum,
 12 litres water,
 500 grammes chlorate of soda,
 1 litre chromate of lead paste,
 1,500 grammes aniline salt.

After cooling add per litre of colour:

30 grammes sulphide of copper paste.

The chromate of lead paste is prepared by dissolving 10 kilos of bichromate of potash in 30 litres of water, and 30 kilos of acetate of chrome in 30 litres of water. Mix the two solutions, filter through a cloth and allow to drain. Then wash the precipitate on the filter with hot water. This gives 35 kilos of paste.

There is no necessity to chrome this black. When it is printed together with steam colours, which require steaming more than 15 to 20 minutes, it should be passed through ammoniacal vapour after development.

3.—VANADIUM BLACK.

This black, which we owe to Georges Witz, is based on the facility with which the salts of vanadium act as oxygen carriers. At first metavanadate of sodium was used; H. Schmid (*D.P.J.*, 251, p. 43) recommended in preference chloride of vanadium. He prepared this by dissolving 20 grammes of metavanadate of ammonia in 100 c.c. of hydrochloric acid and 200 c.c. of water. Reduce at the boil with 15 c.c. of bisulphide of soda, until the blue colouration of the liquid shows that chloride of vanadium is formed. Then bring up the liquid to 20 litres by the addition of water. A litre of this solution represents 1 gramme of metavanadate of ammonia, that is to say, about $\frac{1}{2}$ gramme of metallic vanadium.

In practice very variable proportions of vanadium are used, according to the nature of the goods, and also according to the local price of the salt; from 0.8 gramme to 3 grammes of chloride

of vanadium to 1 kilo of aniline oil or $1\frac{1}{2}$ kilo of aniline salt. The vanadate may be reduced by using 10 grammes of glycerine instead of the bisulphite.

As vanadium black contains the oxygen carrier in a state of solution, it does not keep as well as the sulphide of copper or chromate of lead blacks. It colours very rapidly in the buckets, the more so in proportion as it contains more vanadium. When this colouration is very pronounced the paste must be used with precaution, as the black already formed in the colour paste is not fixed on the fibre, and will bleed on soaping.

One of the great advantages of vanadium black is that it does not contain any metal that can injure colours printed at the same time, either on washing or on soaping. The trace of vanadium which it contains need not be taken into account. It is therefore specially suitable for use together with alizarine red and pink, and for printing over paranitraniline red. The following recipe is currently used:—

6,700	grammes	wheat starch,
1,000	„	dark British gum,
1,000	„	water,
800	„	aniline salt,
150	„	aniline oil,
400	„	chlorate of soda.

Add immediately before using:

500 c.c. chloride of vanadium solution.

The chloride of vanadium solution is prepared by dissolving 8 grammes of vanadate of ammonia in 40 grammes of hydrochloric acid and 80 c.c. of water. Reduce at the boil with 10 grammes glycerine, and bring up to 20 litres by the addition of water.

The solution of chloride of vanadium should be used as dilute as possible, and well stirred, to prevent the oxidation of the colour paste.

Vanadium black can be developed either by ageing or in the oxidation chamber. The black obtained by the above recipe develops perfectly by a passage of two minutes at 95° C, in the Mather and Platt. It is not absolutely necessary to chrome it.

Depierre describes a black specially intended for the printing of goods dyed with alizarine red:—

9,000	grammes	wheat starch,
1,000	„	dark British gum,
95	litres	water,
3,300	grammes	chlorate of potash,
20	„	methyl violet (to mark the pattern).

Boil and add when cold:

6,450	grammes	aniline oil,
5,700	„	hydrochloric acid,
345	c.c.	vanadic solution.

The vanadic solution is prepared with 8 grammes of vanadate of ammonia, 70 grammes of hydrochloric acid, and 8 grammes of

glycerine; heat until the reduction is complete, and add 800 c.c. of water.

This black develops after 24 hours' ageing followed by a passage through the Mather and Platt. The goods are then passed through a chalk bath at 70° C., washed and lightly soaped.

Depierre's black is much weaker than the preceding blacks. It contains only 64 grammes of aniline, 57 grammes of hydrochloric acid, and 33 grammes of chlorate of potash per litre. The quantity of hydrochloric acid employed will neutralise only 45 grammes of aniline.

4.—PRUSSIAN BLACK.

This is certainly the most easily used, and the most employed printing colour. It keeps well, prints easily, and has little or no tendering effect upon the fibre. On the other hand it is not developed as well as the black previously described by ageing or steaming, and requires after-chroming.

Prepared ferrocyananiline is incorporated with the colour paste, or a mixture of aniline salt and prussiate of potash or soda, capable of producing ferrocyananiline by double decomposition, is used instead.

This black is particularly suitable for printing ground-work and for large patterns. It is best developed by a passage for three minutes through the Mather and Platt, at as high a temperature as possible. After this first steaming it will stand a second and longer steaming without pressure. It is not to be recommended for use on oiled cloth. The following is a practical recipe for ferrocyaniline black:—

13 litres	starch paste, 200 grammes per litre,
1 „	gum tragacanth, 60 grammes per litre,
1,000 grammes	aniline salt,
50 „	aniline oil,
2,000 „	ferrocyananiline paste,
150 „	acetic acid,
900 „	chlorate of soda.

This black is developed by a passage through the Mather and Platt, followed by steaming without pressure for twenty minutes. The goods are then passed through soda or soap. Prussiate black may also be obtained with hydrochloride of aniline as follows:—

120 grammes	wheat starch,
80 „	British gum,
45 „	chlorate of soda,
500 „	water.

Boil and add lukewarm:

500 grammes ferrocyanide of potassium.

Then when cold:

85 grammes aniline oil,
112 „ hydrochloric acid, 19° B.

Bring up to 1 litre with water.

The quantity of hydrochloric acid used in this black neutralises 76 grammes of aniline, and consequently 9 grammes of aniline remain free. The 76 grammes of aniline represent 106 grammes of dry hydrochloride. This proportion is rather high. According to requirements the quantity of aniline and the corresponding proportions of chlorate and of yellow prussiate may be reduced. At the most, this black will stand a passage of three minutes in the Mather and Platt. If after this it is necessary to steam it, it must be passed through ammoniacal vapour after going through the Mather and Platt.

Depierre describes another steam aniline black :

12 litres water,
5 „ gum tragacanth paste, 75 grammes per 1,000.
2,400 grammes wheat starch.

Boil and add hot :

1,440 grammes chlorate of potash,
960 „ aniline oil,
2,880 „ aniline salt,
194 „ red prussiate of potash.

This is developed by steaming for fifteen minutes, but it will stand a longer steaming.

E. Kopp describes two steam aniline blacks used by him at Rouen.

Chlorate of Aniline Black I.

1,800 grammes starch,
1,800 „ light British gum,
10 litres chlorate of aniline.

Boil, and add when lukewarm :

1,200 grammes aniline salt crystals,

and when cold :

1,000 grammes sulphide of copper,
2 litres water.

The chlorate of aniline is made by dissolving 2,500 grammes of chlorate of alumina in the same weight of water, and adding 600 grammes of aniline oil. Mix and heat to 40° C.

The chlorate of alumina is made by dissolving 1 kilo of sulphate of alumina in 4 litres of water, and adding 1 kilo of chlorate of barium. Stir up well, allow to settle, and use the clear liquid.

Chlorate of Aniline Black II.

16 kilos starch,
15 „ light British gum,
32 litres water,
96 „ chlorate of aniline.

Boil and add when cold :

3,600 grammes sulphide of copper.

Chlorate of Aniline Black III.

The chlorate of aniline in this case is really a mixture of chlorate and tartrate of aniline. Prepare a solution of 8 kilos chlorate of potash and 8 kilos sal ammoniac in 48 litres of hot water, and another solution of 19 kilos of tartaric acid in 44 litres of water, with the addition of 16 litres of aniline oil. Mix these two solutions, allow to settle, and use the clear liquid.

Tartrate of Aniline Black.

15 kilos	light British gum,
15 litres	water,
2,500 grammes	sal ammoniac,
2,000	„ chlorate of soda,
5 litres	aniline oil.

Boil and add when cold:

2,500 grammes	sulphide of copper paste,
5,000	„ tartaric acid in fine powder.

W. Wendt (*D.C.P.*, 1907, p. 51) claims to have had a long experience in the use of tartaric acid in aniline black printing. His recipe varies little from that given above, but he points out that the amount of thickening must depend on the character of the design to be printed, and the depth of the lines. No thickening at all is used for very fine lines.

DIPHENYL BLACK.

This black was patented on April 4th, 1901 (*D.R.P.*, 134,559) by the Farbwerke vorm. Meister Lucius and Bruning. We quote the specification in extenso of the British patent (*E.P.*, 15,062-1901).

The black hitherto produced by dyers or printers by oxidation or steaming has the disadvantage that it easily turns green, as the action of dilute acids contained in the perspiration, or still more that of reducing agents, such as sulphurous acid found in the air, and especially in storehouses, produces a greenish hue like that of emeraldine, the intermediate product in the formation of the black. This greening often occurs to a disagreeable extent in the case of wearing apparel dyed with aniline black.

This drawback has been avoided to a certain degree, but an aniline black which does not absolutely turn green has not been obtained hitherto. Besides, the aniline black has this drawback, that cotton fibre is easily attacked, and thus becomes rotted by the quantity of acid requisite for the formation of the black.

The present invention relates to the manufacture of a black by substituting for the aniline generally used, primary, secondary, or tertiary amido or amido-oxy-derivatives of the diphenylamine series, and oxidising these bodies on the fibre. A full, deep black may be thus obtained which does not become green, and does not attack the fibre. The following compounds have proved specially suitable for this purpose:—paramidoparaoxydiphenylamine, paramidoparaoxyphenyltolylamine, dimethylparamidoparaoxydiphenylamine, dimethylparamidoparaoxyphenyltolylamine, diphenylamine, diamidoparaoxydiphenylamine and dimethyldiami-

dodiphenylamine, and this invention relates to the manufacture of a black by oxidation or steaming from these and like bodies. In like manner may be used any other primary secondary or tertiary amido or amido-oxy-derivative of the diphenylamine series or homologues of the series, except such as have the alkyl group in para position to the imide group.

Of these compounds only about one-third of the quantity necessary in the case of aniline is required for a full deep black, and whereas in the case of aniline, besides oxidising agents, a carrier of oxygen is necessary, such as a solution of a vanadium salt, potassium ferrocyanide, copper sulphide, etc., the formation of the black occurs here so readily that the use of a carrier of oxygen may be dispensed with, its application, however, not being absolutely excluded. A drawback caused by potassium ferrocyanide, which is commonly used, is avoided by this new process, namely the formation of Prussian blue, which gives to the black when it leaves the steam a very beautiful bluish tint, which disappears, however, and owing to the formation of hydrated peroxide of iron, gives place to a less beautiful brown-black when the goods are treated with soap and sodium carbonate. Besides, the new process has the hygienic advantage of avoiding the vapours of prussic acid, which are evolved in the manufacture of the black by the old process.

A further drawback of the potassium ferrocyanide consists in the impossibility of printing this compound beside alizarine-aluminium colours, as the shades of the latter are much injured by the proximity of the iron compound. As no such compound is used in the new process, the new black may be used together with all colours obtained by steaming.

The readily oxidisable bases used in this process, and the small quantity of acid they require to form the black, are also of special technical value, as it allows of the colour being directly developed while the piece-goods are passed over the drying cylinders immediately after padding. The slow process of drying in the hot-flue and the passing through the steam apparatus, or the prolonged spreading out in the oxidation chamber, are thus avoided. The new black is very fast to soap, sodium carbonate, light, sulphur and acid, as well as to alkali and ironing. The black may be produced on half-silk and silk as well as on cotton.

Black Printing Colour I.

- | | |
|--------|--|
| 30 | grammes of paramidoparaoxydiphenylamine or the |
| | equivalent quantity of any other of the |
| | aforesaid bases, |
| 100 | „ acetic acid 8° B., |
| 8 c.c. | hydrochloric acid 22° B., |
| 600 | grammes acetic thickening, |
| 30 | „ sodium chlorate, |
| 232 | c.c. of water. |

Black Printing Colour II.

30	grammes	paramidoparaoxydiphenylamine or the equivalent quantity of any other of the aforesaid bases,
100	„	acetic acid 8° B.,
30	„	acetine,
600	„	acetic thickening,
60	cc.	aluminium chlorate 22° B.,
180	„	water.

After printing, the goods are dried, steamed for 3 minutes, washed and soaped.

Padding Colour I.

30	grammes	paramidoparaoxydiphenylamine,
300	„	hot water,
10	c.c.	hydrochloric acid 22° B.,
100	grammes	acetic acid 8° B.,
100	„	tragacanth water (60 grammes per 1,000 c.c.)
30	„	sodium chlorate,
500	„	water.

Padding Colour II.

30	grammes	paramidoparaoxydiphenylamine,
100	„	acetic acid 8°,
30	„	acetine,
100	„	tragacanth water (60 grammes per 1,000 c.c.)
70	c.c.	aluminium chlorate 22° B.,
500	grammes	water.

After padding, the cloth is dried in the hot-flue and steamed in the Mather and Platt for 3 minutes, or the black is directly developed on the hot drying cylinders.

As we have already said, paramidodiphenylamine is the Diphenyl Black Base of commerce. The Farbwerke vorm. Meister, Lucius and Bruning state that all that is necessary is to add chloride of aluminium and chlorate of soda to the Diphenyl Black Base, dissolved in acetic acid to obtain a printing colour, and all fear of tendering the fibre is obviated. The black also is perfectly ungreenable. It requires no subsequent chroming, and does not give off the unhealthy vapours of aniline and prussic acid, which have been found a drawback in using ordinary aniline black. These vapours are troublesome, not only from the hygienic point of view, but because they stain bleached vegetable fibre yellow.

Diphenyl Black Base is dearer than aniline, but 30 grammes of this product per litre of colour paste gives a fine black. Its good qualities have enabled it to be employed with success for padding, and for large patterns, and it is easily used together with steam colours. The Farbwerke give the following directions for its use:—

Diphenyl Black Base is only slightly soluble in water, but dissolves easily in acetic acid or acetine. It dissolves equally well

in the other acids, such as hydrochloric, tartaric and oxalic acids, but the salts produced crystallise out on cooling, and therefore these acids are troublesome to use. The majority of the usual oxidants can be employed with it, the best results have been obtained with the chlorates of soda and of alumina, and with the salts of copper. Printing colours made with sulphide of copper paste will keep for some days. On the other hand, when the colour is prepared with chloride of copper, this salt must be used in a very dilute state, and added to the printing paste immediately before printing, in order to avoid the premature formation of the black.

Chloride of copper printing paste is recommended specially for yarn printing (rainbowing) because of the rapidity with which it oxidises on drying, thus obviating the necessity of steaming. When this colour is to be machine printed, one gramme sulphocyanide of potassium per litre should be added to the thickening to prevent the printing paste from attacking the doctors.

Yellow prussiate should not be used as oxygen carrier, as it precipitates the Diphenyl Base. The salts of vanadium cannot be recommended, as they produce a rapid oxidation in the printing colour. When chloride of aluminium is used, it produces chlorate of aluminium by double decomposition with the chlorate of soda in the printing colour, and this with the salt of copper oxidises the base rapidly and converts it into a fine blue black.

When the black is printed together with alizarine reds and pinks on oiled cloth, the proportion of chloride of aluminium should be increased somewhat to prevent the oil from acting as a reserve. This black will stand steaming for an hour, or even more, without the shade changing or the fibre becoming tendered.

After printing the colour should appear a light grey and must not be dried too sharply. Steam in the Mather and Platt at 95 to 102° C. The goods are not after-chromed, as this gives the black a brownish tinge, but are passed through a hot alkaline soap bath and rinsed.

To make comparative trials, a pattern of Diphenyl Black, and a pattern of aniline black were steeped at the same time at 35° C., in a solution containing 44 c.c. bisulphite of soda, 36° B., and 40 c.c., hydrochloric acid, 22° B. They were left for ten minutes. The aniline black turned green while still in the solution, and much more after drying, whereas the Diphenyl Black was unchanged.

1.—*Diphenyl Black Base I. with Copper Sulphide.*

6,000	grammes	acetic acid starch thickening,
200	„	olive oil,
300	„	sodium chlorate,
500	„	water,
350	„	Diphenyl Black Base I.,
	1 litre	acetic acid, 6° B.,

300	grammes	lactic acid, 50 per cent.,
180	„	aluminium chloride, 30° B.,
150	„	copper sulphide paste, 30 per cent.,
20	„	ammonium vanadate, 1: 1,000,
1,000	„	water.

2.—*Diphenyl Black Base I. with Cerium Chloride.*

As No. 1, except that the copper sulphide is replaced by the same weight of cerium chloride 20 per cent.

These two printing colours are intended especially for thin tissues, where the least weakening is injurious and a long steaming of one hour is required on account of the other dyes present. The drying after printing must not be too sharp. The goods are then steamed first from 1 to 3 minutes in the Mather and Platt, and then for one hour in the steam chest, passed through a bath containing 3 grammes of soda and 2 grammes of soap per litre and rinsed.

3.—*Diphenyl Black Oil DO with Copper Sulphide.*

1,100	grammes	wheat starch,
5,315	„	water,
1,125	„	acetic acid, 6° B.,
200	„	olive oil.

Boil half an hour and add the oil warm. On cooling add

250	grammes	sodium chlorate,
500	„	Diphenyl Black Oil DO,
2.25	„	lactic acid, 50 per cent.,
123	„	hydrochloric acid, 18° B.,
67	„	water.

Immediately before use, add

200	grammes	copper sulphide paste, 30 per cent.,
630	„	water,
215	„	aluminium chloride, 30° B.

This printing colour is the one most commonly used both for ground patterns and in topping goods which are not too thin.

4.—*Diphenyl Black Oil DO with Ferricyanide.*

6,300	grammes	acetic starch thickening,
300	„	sodium chlorate,
600	„	water,
500	„	Diphenyl Black Oil DO,
1	litre	acetic acid 6° B.,
300	grammes	lactic acid, 50 per cent.,
100	c.c.	hydrochloric acid, 22° B.,
200	„	water,
200	grammes	aluminium chloride, 30° B.
108	„	potassium ferricyanide,
402	„	water.

Printing colours Nos. 3 and 4 must not be dried too sharply; they are steamed from one to three minutes in the Mather and Platt, and passed direct without chroming through a bath at 60 deg. C., containing 3 grammes of soda and 2 grammes of soap per litre and rinsed.

The use of aniline black with ice colours is of special interest. It is well known that no black is obtained by printing with aniline black on goods prepared for paranitraniline with beta naphtholate of soda, even if the printing colour is acid enough to neutralise the alkalinity of the bottom colour.

M. Richard (*B.S.M.*, 29th May, 1908) found that if Diphenyl Black Base I. is added to the aniline black and printed on the naphthol prepared goods, a very fine deep black can be obtained together with para red or other diazotised bases.

63,800	grammes	acid starch thickening,
4,500	„	aniline salt,
4,500	„	Diphenyl Black Oil DO,
4	litres	acetic acid, 6° B.,
4	„	lactic acid, 50 per cent.,
1.2	„	hydrochloric acid, 21° B.,
3,500	grammes	sodium chlorate,
9	„	water,
1,500	„	copper sulphide paste, 30 per cent.,
1,500	„	water,
1,500	„	aluminium chloride, 30° B.,
1	litre	aluminium vanadate, 1 : 1,000.

Paraphenylenediamine itself acts in the same way as phenyl-paraphenylene and the other diphenylamine derivatives mentioned in D.R.P. 134,559 of the Farbwerke Hoechst. A further use of aniline black in para red and aniline black styles is mentioned in another patent of the same firm. According to this process, the black is printed on the naphthol prepared goods, steamed in the Mather and Platt, and then at once dyed in nitraniline solution. In contrast to the earlier methods of developing the aniline black first on white goods, and then rinsing before impregnating and dyeing, or of printing only on goods already dyed, the new process is cheap and simple, as several rinsing, soaping, and drying operations are saved.

This result is achieved by a combination of Diphenyl Black Base, paraphenylenediamine, and aniline salt, and there is no necessity to make the printing colour strongly acid.

The black prepared by the following recipe is printed on naphthol impregnated goods, steamed one minute in the Mather and Platt, dyed at once in paranitraniline and rinsed.

Diphenyl Black on Naphthol Prepared Goods.

500	grammes	gum tragacanth, 60 : 1,000,
100	„	China clay paste, 1 : 1,
58	„	aniline salt,
16	„	Diphenyl Black Base I.,
5	„	paraphenylenediamine,
12	„	aniline oil,
50	„	acetic acid, 6° B.,
20	„	aluminium chloride, 30° B.,
30	„	sodium chlorate,
71	„	water,
20	„	copper sulphide paste, 30 per cent.,
105	„	water,
15	„	ammonium vanadate, 1 : 1,000.

Naphthol Grounding.

25	grammes	beta naphthol,
25	„	caustic soda lye, 40° B.,
20	„	para soap P.N.,
3	„	tartar emetic,
5	„	glycerine.

As this printing colour is not very acid, no pale edges form round the black. It also gives a very fine deep black side by side with paranitraniline red printed on naphthol prepared goods.

Padding Bath.

100	grammes	gum tragacanth paste, 60 grammes per litre,
200	c.c.	water.
30	grammes	Diphenyl Base, dissolved in
200	c.c.	acetic acid, and
20	grammes	acetine
30	„	chlorate of soda,
100	c.c.	water,
15	„	chloride of aluminium,
100	„	water.

Immediately before use mix with this 4 c.c. chloride of copper, 40° B., in 300 c.c. water, and bring up to one litre. Stir well, pad on and develop on the cylinders, dry without steaming, wash, soap and dry.

The drying may be done in the hot room on leaving the padding machine, followed by development for one or two minutes in the Mather and Platt.

Printing colours Nos. 1 and 2 made with pure Diphenyl Black Base I. are absolutely ungreenable and do not tender the fibre, but are dearer than aniline black on account of the high price of Diphenyl Black Base I.

Printing colour No. 3, made with Diphenyl Black Oil DO is as cheap as a Prud'homme aniline black.

Wool and silk are easily printed and dyed with Diphenyl Black. For silk and half silk the processes are the same as for cotton. Wool and half wool require neither chloring nor souring, both necessary with aniline black. The wool is soaked thoroughly in boiling water, and this is all the preliminary treatment required.

The following recipe gives a padding bath suitable for all fabrics.

- A. 600 grammes Diphenyl Black Oil DO, and
 1,200 c.c. acetic acid, 6° B.; stir into
 1,200 grammes gum tragacanth, 20 : 1,000.
- B. 1,200 grammes gum tragacanth, 20 : 1,000,
 330 c.c. hydrochloric acid, 19° B.,
 30 ,, aluminium chloride, 30° B.,
 200 ,, chromium chloride, 30° B.,
 40 ,, copper chloride, 40° B.,
 1,100 ,, water.
- C. 300 grammes sodium chlorate,
 1,900 ,, water.

Just before use, solutions B. and C. are poured into A. The colour is thinned, if necessary, with the following paste:—

- 300 grammes tragacanth, 20 : 1,000,
 150 c.c. acetic acid, 6° B.
 550 ,, water.

ANILINE BLACK AND STEAM COLOURS.

Logwood black in many cases is replaced by the sulphide of copper, chromate of lead, or prussiate black, which are particularly suitable for articles which must be fairly fast and resist frequent washing. For delicate mode styles, logwood black so far has always been used. It seems likely, nevertheless, that the diphenylamine black will replace all others in these styles, and also in all styles in which black is associated with steam colours, owing to the fact that Diphenyl Black can support a long steaming without danger to the fibre and without a preliminary passage through ammonia vapour. Moreover, it has all the good qualities of aniline black.

When sulphide of copper is used it is indispensable to pass the goods through ammonia after development in the Mather and Platt. Chromate of lead and prussiate black will stand a fairly long steaming, which may extend to half an hour, but the accompanying colours risk being damaged by the aniline and acid vapours which are given off, and at the same time they are fixed badly or not at all in the parts which touch the black of the pattern. Some colours, Methylene Blue, for instance, are so changed by steaming together with aniline black that the light blues turn to a dirty grey. To avoid this logwood black must be used.

BLACK AND CHROME ORANGE.

Kiellmeyer recommends for this favourite style the use of a nitrate of aniline black to prevent the formation of chloride of lead in the course of printing. This results from the action of the lead salts of the first roller on the hydrochloride of aniline of the second, and it is objectionable as it clogs the engraving.

E. Kopp, at Rouen, prints any aniline black together with orange N.

Orange N.

1 litre Orange No. 2,
2,000 grammes washed sulphate of lead.

Orange No. 2.

48 litres basic acetate of lead, 26° B.,
4,500 grammes white starch,
4,500 „ British gum; boil and add
6,000 „ basic acetate of lead.

Basic Acetate of Lead.

36 litres water,
15,000 grammes acetate of lead, heat to the boil and add
3,000 „ litharge.

Continue to boil for half an hour, leave it to settle for 12 hours and use the clear liquid.

The black and the above colour are printed on, allowed to oxidise for a night, passed through ammonia in a bath containing 600 litres of water and 25 litres of ammonia, rinsed for ten minutes, and chromed with 3 kilos of bichromate of soda or potash in 700 litres of water. Six pieces of 120 metres at a time are run through this for twenty minutes, then washed and passed at full width through a bath of 2 kilos of quicklime in 2,500 litres of boiling water. When six pieces have passed through this bath it is reinforced with 350 grammes of quicklime. The goods are then washed once more, hydro-extracted, rinsed and dried.

Kopp also uses at Rouen the following nitrate of aniline black:—

27 litres water,
4,750 grammes white starch,
3,000 „ light British gum.

Boil, shut off steam and add:—

2,000 grammes chlorate of soda,
1,150 „ sal ammoniac.

This gives 32 litres, add when cold,

2,525 grammes aniline oil,
2,475 „ nitric acid,
1,900 „ sulphide of copper.

The passage through ammonia can be replaced by a passage for two minutes through carbonate of soda.

Kiellmeyer obtains a very bright orange by treating the pieces printed in black and yellow by the following process:—The pieces pass through a continuous dyeing machine. The first compartment contains 30 to 50 litres of ammonia in 970 litres of water. The second contains 25 kilos of soda crystals in 1,600 litres of water, heated to 40° C. The strength of the bath must be kept up as the pieces pass through. Before the cloth goes into the soda bath it should make a long traverse over the top of the first compartment in order to utilise the ammonia gas with which the air is saturated.

When the black and the orange touch in the patterns, Kiellmeyer recommends that the basic acetate of lead in the printing paste should be replaced by a mixture of acetate of nitrate or by basic nitrate. If instead of chrome orange it is desired to obtain chrome yellow the lime bath is not used.

Depierre recommends for the lime bath 1,500 litres of water, 7 kilos of lime, and 1,800 grammes of bichromate of soda.

Great care must be taken in printing the acetate of lead colour. A water roller should be placed between that which prints the orange and that which prints the aniline black.

BLACK AND IRON BUFF.

This is the style used for handkerchiefs. For the black the sulphide of copper black is preferably used or a prussiate black rich in aniline, capable of being sufficiently developed by a passage of three minutes through the Mather and Platt and by an alkaline bath to fix the iron in order to avoid the necessity of chroming.

The buff colour is made by mixing equal parts of acetate of iron, 12° B., and British gum water. It can be diluted according to requirements by adding thickening. The acetate of iron is obtained by double decomposition between sulphate of iron and acetate of lead. After passing the goods through the Mather and Platt, they are aged for a night and the oxide of iron is then fixed by passing through cold soda lye at 3° B. The goods are thoroughly washed and soaped. The soda bath can be replaced by a passage through a hot bath containing 20 grammes of ammonia per litre, or by a passage through a boiling bath containing 30 grammes of lime per litre. This style can be combined with albumen colours, and in this case either the ammonia or the lime bath must be used.

Iron buff is easily discharged by acids.

BLACK WITH ALUMINIUM AND IRON MORDANTS.

Aniline black was used for this very important style from the very commencement of its appearance as a printing colour. Its employment for this purpose was greatly extended a few years later when artificial alizarine was discovered.

The goods are thoroughly bleached in order to get an irreproachable white, and printed with a sulphide of copper black, and with iron or aluminium mordants, alone or mixed together.

Aluminium Printing Paste.

100	grammes	wheat starch,
100	„	light British gum,
50	„	acetic acid,
$\frac{1}{2}$	„	magenta (to mark the pattern),
30	„	glycerine,
500	„	water.

Boil and add when cold

300 c.c. acetate of aluminium, 10° B.,

10 grammes tin salts.

Bring up to 1 litre with water.

After printing the goods are dried thoroughly and passed through the Mather and Platt at 70° C., or aged by exposure for a day.

The goods are then passed as usual through cow dung or phosphate of soda, or where the use of the salt is allowed, they are dunged with arseniate of soda, washed thoroughly and dyed with alizarine. To clear the white a bath of bran water is given after dyeing. The goods are dried, passed through soluble oil, steamed two hours without pressure, and soaped in rope form, sometimes with the addition of stannate of soda.

The red is shaded towards a dark brown by adding varying quantities of iron to the aluminium mordant.

BLACK OVER A RED GROUND.

This style is obtained in the same way whether the bottom is alizarine red or paranitraniline. The vanadium black is used, as a copper or iron black darkens either red.

Maslowski (*F.Z.* 1896, p. 33) describes the following black used in Russia for printing over Turkey red:—

40,000	grammes	thickening A,
3,600	„	hydrochloride of aniline, in
2	litres	water,
800	grammes	vanadate of ammonia solution.

Mix well and pass twice through a tight cloth filter.

For heavy designs and ground work, this black should be diluted with British gum water.

Thickening A.

22,000	grammes	wheat starch,
150	litres	water,
8,800	grammes	chlorate of potash.

Boil, and add when lukewarm

7,300 grammes sal ammoniac.

Stir until the mixture cools.

Vanadate of Ammonia Solution.

100 grammes vanadate of ammonia,
58 litres hot water.

This vanadium black is a good printing colour over paranitraniline red. The black for printing over a red ground should be rich in aniline, so as to cover the ground completely. As a rule, the aniline black and paranitraniline red style is at its best when a very full prussiate black is printed to begin with, developed, chromed, soaped well and washed. The goods are then padded with naphthol and dyed.

BLACK OVER A NAPHTHOL GROUND.

Aniline black goes badly on fabric prepared with naphthol; on the one hand the naphtholate of soda interferes with the development of the black, and on the other hand the acidity of the printing colour causes the formation of aureola, or colour halos, which take only a pale yellowish red on the subsequent dyeing in nitrodiazobenzene. If the proportion of acid and of chlorate in the printing colour is increased so as to saturate the naphtholate of soda and to oxidise the naphthol, the development of the black is hardly improved and the aureola are still more accentuated.

To assure the success of the reserve style with paranitraniline red it would be of great interest to be able to use the aniline black together with a reserve. The sole practical method of doing this consists in printing aniline black and a paste forming a reserve, then developing the black, padding in a solution of naphtholate of soda with as little caustic soda as possible in excess, and then dyeing. To prevent the reserve paste from running, the goods are passed through a pair of squeezing rollers, the lower one of which rotates in the naphthol bath. For the same purpose the drying is done on the cylinders. Good white effects are obtained in this way. The colour reserves are not very fast to washing. A good white reserve can be obtained as follows:—

150	grammes	pipe clay,
100	c.c.	water,
250	grammes	stannous oxide paste,
50	„	tin salt,
40	„	tartaric acid,
50	„	citrate of ammonia,
40	„	Turkey red oil,
30	„	glycerine,
290	„	dark British gum paste.

J. Koechlin and J. Langer (*B.S.M.*, 1899, p. 74) propose to use tannin for the colour reserve. From 200 to 400 grammes of tannin per litre are added to the colour reserve, this is printed on bleached material, steamed an hour, then passed through naphtholate of soda as above, or is padded on in the printing machine, this

style is difficult to work successfully and has not been adopted. The only method which should be followed is to print aniline black over the finished red, and at the same time white and colour discharges prepared with hydrosulphite formaldehyde.

BLACK OVER A TANNIN GROUND.

As tannin forms a reserve under aniline black, this must be obviated by the use of a much larger quantity of chlorate and of aniline salt in the colour paste. The goods must also have a longer steaming or be given two passages through the Mather and Platt in order that the black may be completely developed. As oxygen carrier sulphide of copper should be chosen, and of course the goods will not stand chroming.

Pluanzski (*B.S.M.*, 1897, p. 98) describes a style of his own in which he combines the effects of conversion and superposition. A white reserve containing tin salts and acetate and tartrate of soda is printed on a white fabric or over material dyed with the diamine colours. Then over this is printed a prussiate aniline black to which basic colours are added. The white discharge cuts the diamine colour; and the tartrate of tin, which is formed in the white, reserves the aniline black printed over it, and with the aid of the prussiate fixes the basic colour contained in the black printing paste.

White Reserve.

218	grammes	gum tragacanth,
100	„	tartaric acid crystals,
100	„	water,
46	„	calcined carbonate of potash,
66	„	caustic soda, 45° B.

Verify the neutrality of this paste, then prepare a second paste with:—

170	grammes	gum tragacanth,
120	„	tin salts.

Mix these two pastes thoroughly by grinding, then add:—

60	grammes	soda ash,
100	„	acetate of soda crystals,
10	„	oleine,
10	„	turpentine.

Black with Green.

1000	grammes	thickening for black,
20	„	Brilliant Green,
80	„	glycerine,
90	„	aniline oil,
90	„	hydrochloric acid, 19° B.

Black with Red.

1000	grammes	thickening for black,
30	„	Rhodamine 6G,
100	„	glycerine,
110	„	aniline oil,
110	„	hydrochloric acid 19° B.

Thickening for Black.

110	grammes	white starch,
550	„	British gum 25 : 100,
117	„	water.

Boil together, then add:—

45	grammes	chlorate of soda,
130	„	water,
48	„	yellow prussiate,
100	„	water.

E. Cabiati (*E.P.*, 14,704, 1895, *D.C.P.*, 1896, p. 12) in order to save indigo, prints the goods before dyeing in the vat with a fine network of aniline black. This cross-hatching gives the dyed goods a perfectly uniform velvety appearance without losing any of the bloom, and lends the illusion of a very dark indigo dyeing.

A. G. GREEN'S PROCESS.

A. G. Green (*E.P.*, 16,189, 1907) patented a process in which the oxidation of the aniline is effected solely or mainly by the oxygen of the air. The possibility of dispensing with an oxidised agent and thus of avoiding the tendering of the fibre, depends on the discovery that the addition of a small quantity of a paradiamine or of a para-amidophenol to a mixture containing aniline and an oxygen carrier, such as a salt of copper, greatly accelerates the oxidation of the aniline by atmospheric oxygen.

In the ordinary processes of producing an aged black the quantity of mineral acid employed cannot be materially reduced below the proportion of one equivalent to one equivalent of base, but under the new conditions a mixture which is strongly basic, containing, for instance, as little as half an equivalent or less of hydrochloric acid, may be used with satisfactory results. Moreover, the hydrochloric acid or other mineral acid may be wholly or in part replaced by an organic acid, such, for instance, as formic acid, without materially affecting the quality of the black obtained. In either case, whether a basic mixture is employed or a mixture containing an organic acid, the tendering of the fibre by free mineral acid liberated during ageing or steaming is avoided, even when these operations are unusually prolonged. As oxygen carriers, the chlorides of copper have been found to give the best results, and in order to prevent the premature formation of oxidation products in the mixture, it has been found preferable to employ the copper in

the form of a cuprous salt. A convenient method of effecting this is to add cupric chloride to the mixture, together with a sulphite or bisulphite in quantity sufficient to reduce the cupric salt to the cuprous state, and a sufficient amount of a soluble chloride, such as sodium, potassium, or ammonium chloride, to keep the cuprous chloride in solution. Mixtures thus prepared are quite stable, and remain clear and colourless on exposure to air for a considerable period. As in the ordinary method of producing aniline black, the aniline may be replaced wholly or in part by toluidine or metaxylidine.

The mixtures are applied to textile fibres and fabrics in the usual manner by padding or printing. In the latter case the mixture is thickened. The black is then developed by exposure of the material to air, which may be effected either by passage through the ordinary rapid ager, by hanging in a moist atmosphere, or by steaming. Finally the material is washed and dried, or subjected to a final oxidation by means of bichromate, or to any other after-treatment which is deemed desirable either to modify the shade or to render the black less liable to green.

Amongst the paradiamines and para-amidophenols suitable for this purpose are: Paraphenylenediamine and its sulphonic and carboxylic acids, para-amidophenol, dimethylparaphenylenediamine, dipara-amidodiphenylamine, benzidine, diamidodiphenylmethane, quinone monoimide, quinone di-imide and their chlorides, paranitrosophenol, nitrosodimethylaniline, para-amidophenylquinonimide, and their analogues, homologues, or derivatives. The following are examples:—

1. The padding mixture is prepared by adding a solution composed of 48 pts. cupric chloride, 140 pts. ammonium chloride, and 14 pts. sodium meta-bisulphite in 500 pts. cold water, to a solution composed of 50 pts. aniline, 2 pts. paraphenylenediamine, 15 pts. hydrochloric acid (30 per cent.), and 15 pts. formic acid (90 per cent.) in 1,500 pts. cold water.

2. The padding mixture is prepared by adding a solution prepared as in example 1 to a solution composed of 50 pts. aniline, 4 pts. paraphenylenediamine, 30 pts. formic acid (90 per cent.) in 1,500 pts. cold water.

3. The padding mixture is prepared by adding a solution prepared as described in the first part of example 1 to a solution composed of 50 pts. aniline, 4 pts. paraphenylenediamine, and 50 pts. hydrochloric acid (30 per cent.) in 1,500 pts. cold water.

It is claimed that by the new process a fuller utilisation of the aniline is rendered possible, the danger from spontaneous inflammation is removed, the risk of injury to the workpeople is greatly diminished, the manufacture is simplified, and greater speed of production is attainable. The action of the paradiamine or para-amidophenol is believed to be catalytic, since the quantity employed need only be small in proportion to the aniline, and may be varied within wide limits. It is thought that these substances bring

about the oxidation of the aniline by intermediate formation of complex indamines, from which they are constantly regenerated.

E. Knecht (*J.S.D.C.*, 1908, p. 230) says that this discovery may be regarded as the most important in the history of aniline black since it was first introduced by Lightfoot in 1863, its most salient feature being the complete omission from the padding liquor of any oxidising agent. From the researches of Willstaetter and Moore we know that emeraldine, when heated to 150° C., is converted into aniline black on the one hand, and the leuco base of emeraldine on the other. The latter is converted by air oxidation again into emeraldine, so that it had been shown to be possible to effect the last stage of oxidation (in the laboratory) by means of atmospheric oxygen. The new process constitutes a very important advance, inasmuch as the whole of the oxidation is effected by the air.

Two patterns illustrating this process will be found at the end of this volume.

CHAPTER VI.--Resists and Discharges.

Shortly after the discovery of aniline black, a method was sought of decorating the dyeings with white and coloured effects. The first attempts were based on the principle that the black is developed only in the presence of an acid, whether free or produced by the splitting up of salts, and that the presence of an oxidant is also necessary. Alkaline or reducing agents were therefore employed to prevent the development of the black in parts of the cloth.

Good results were obtained, but these styles did not become general until Prud'homme brought out a process which allowed fabric padded through an aniline black bath to be operated upon. By his process the cloth could be dyed uniformly on both sides, and decorated at will with white or with colours. Up to this time it had been possible only to slop-pad the goods, first printing a single face with the reserve paste.

Storck and Strobel noted that the sulpho-cyanides are transformed into persulphocyanogene by the compounds of chlorine with oxygen. As these compounds are used in the formation of aniline black, the black can be completely reserved by adding a sulphocyanide to the printing paste in the proportion of 50 grammes per litre of gum water.

Colour resists can be printed under aniline black in the same way by adding 50 to 60 grammes of a sulpho-cyanide per litre of albumen or tannin colour. Sulphocyanide of lead was found successful in the case of acid printing colours. Storck gives the following examples of a green:—

3½	litres Methyl Green printing paste,
120	grammes sulphocyanide of potassium,
60	„ acetate of lead,
200	c.c. water.

The basic colours are fixed by the sulphocyanide of lead and by the preliminary oiling of the cloth.

H. Schmid (*D.P.J.* 251, p. 41) referring to this process notes that it had long been known that the sulphocyanides are changed into persulphocyanogene by the action of chlorates. He argues that in the use of the sulphocyanides as resists under aniline black the

persulphocyanogene is not fully formed, as if this were so a white would not be obtained, but a yellow resulting from the formation of insoluble canarine. In his opinion the sulphocyanides absorb a considerable quantity of chlorine before turning into persulphocyanogene, and this intermediate product is soluble and colourless.

Schmid and E. Schweizer state that the xanthates reserve equally as well as the sulphocyanides.

Glenck (*D.P.J.* 241, p. 399) gives very precise instructions concerning the use of the sulphocyanides as resists under aniline black. A solution of 60 grammes of sulphocyanide of potassium or of ammonia per litre of gum water is printed on, and over this aniline black is printed and aged for a night at 30° C. and 26 hygrometric degrees. This process is as successful with colour resists as for whites. For the former it is merely necessary to add basic colours and tannin. After printing on the colour resist, the goods are steamed for an hour; the aniline black is then printed on and developed as above. The goods are then passed through a bath of emetic, washed and lightly soaped.

Witz (*B.S.R.* 1881, p. 206) has studied the action of various bodies on the formation of aniline black. Cyanide of potassium only retards the formation of the black; 100 grammes of yellow prussiate per litre reserves vanadium black, and in this case dextrine is the best thickening. Witz found that albumen, cutch, chalk and zinc dust would also act as reserves. He obtained the best results by using a reserve thickened with white dextrine, and containing 300 grammes of acetate or hydrosulphite of soda per litre.

Romann discovered the tannin resists. He printed a basic colour with 250 grammes of tannin and a small quantity of sulphocyanide per litre, steamed the goods for an hour, and padded or slop-padded on the aniline black. This process has not found practical employment.

Lauber recommended citrate of soda, glucose and caustic soda as a resist.

H. Koechlin sent to the Chemical Society of Paris in 1881 a pattern printed by C. Brandt with alizarine red and pink, and also with Guignet's green fixed with albumen, reserved by sulphocyanide under printed aniline black. H. Koechlin noted that pyrogallie acid in the proportion of 15 to 20 grammes per litre also reserved well.

Kiellmayer (*D.P.J.* 1873, p. 203) obtained a good red resist under printed aniline black by using aluminate of soda, which had already been tried by him as a white resist. For a white, however, this salt was found unsuitable. The white was stained by the aluminium fixed on the fibre. For red reserves, however, it was found excellent, and is still used in handkerchief printing. On these goods it allows large patterns in red to be obtained, and can equally well be applied to Prud'homme's black on padded cloth.

Kiellmayer recommends the following process for the preparation

of the aluminate of soda. Hydrate of alumina is dissolved at the boil in caustic soda at 36° B., rather more lye than the theoretical quantity being used, allowed to settle, and diluted to 24° B. with water. The aluminate thus obtained is kept in well stoppered stoneware carboys in order to prevent the formation of carbonate. It is not sufficiently alkaline to reserve the black completely when it has been sufficiently reduced to act as a mordant for red, and therefore a little caustic soda is added to the printing paste. This is prepared with 7 litres of aluminate of soda at 24° B. diluted with $3\frac{1}{2}$ litres of water thickened with 3,400 grammes of dark British gum, with the addition of about half a litre of caustic soda.

When the aniline black is printed on, the goods are aged and dunged in a bath containing 10 kilos. of sal ammoniac, 5 kilos. of soda crystals, 15 kilos. of chalk, and the usual quantity of cow-dung per 2,000 litres of water. When the goods have passed through, the bath is reinforced with 100 litres of dung, 500 grammes of sal ammoniac, 500 grammes of soda crystals, and 500 grammes of chalk. The goods are dunged a second time in rope form, washed thoroughly, and dyed with alizarine.

This alkaline resist gives a good red, but it has the fault of easily bleeding on ageing. This is prevented by fixing the black in the Mather and Platt, and using as neutral aluminate of soda as possible, reserving the black by acetate of soda or other salts that do not cause bleeding. For the dung bath it is often sufficient to run the goods through a bath containing 50 grammes of sal ammoniac per litre. The bath is reinforced with sal ammoniac in such a manner as to keep it neither acid nor alkaline in order to prevent the alumina already fixed from dissolving.

As we have already said, the alkaline colour paste made with aluminate of soda is also used for a padded prussiate black. In this case the dunging bath must contain soda, in addition to sal ammoniac.

E. Kopp used the following hyposulphite of soda resist for red :

Red Resist.

10 litres aluminium mordant, 16° B.,
3,000 grammes gum arabic,
1,500 ,, hyposulphite of soda.

Print on and dry, print over with aniline black, oxidise and finish as usual. Dye in alizarine, steam and soap.

Aluminium Mordant.

4,200 grammes pure alum,
3,600 ,, pyrolignite of lead,
6 litres water.

An excellent resist is obtained by adding 40 grammes of sulphonyanide of potassium per litre of this aluminium mordant.

When it is desired to combine a white resist with this red resist,

Kielmayer recommends arsenite of soda as alkali and reducing agent. This is prepared by dissolving 4,800 grammes of white arsenic in 4 litres of caustic soda, 36° B. and 4 litres of water. Arsenite of soda is very poisonous, and its use is forbidden in some countries on this account; phosphites of soda could possibly be used in its place. This liquid, which marks 60° B., serves to prepare the white resist under the black. It is diluted with about three times its volume of water, and thickened with dark British gum.

Lauber uses a white resist containing lemon juice, caustic soda and soda, thickened with dark British gum. For the red he uses the following resist:—

10 litres aluminate of soda,
3,500 grammes British gum,
500 ,, olive oil.

To prevent the aureola which are easily produced between the red and the black, Lauber first heats the cloth by a passage over the drying cylinders before printing on the resist. A sulphide of copper black is over printed, and fixed by ageing for four days at 30° C. and 25 hygrometric degrees. It is dunged at 50° C. in the following bath:—

5,500 litres water,
320 ,, cow dung,
50 kilos chalk,
2½ ,, sal ammoniac.

The passage lasts a minute. For each 600 metres of cloth, 500 grammes of sal ammoniac are added. The goods are dunged again in rope form, washed, dyed in alizarine, washed, oiled, steamed for 25 minutes at half an atmosphere, soaped for half an hour at 75° C., washed and dried.

To brighten the red, Lauber uses the following rust bath:—

600 litres water,
400 to 500 grammes rust prepared by dissolving,
1,000 ,, tin salt, added gradually to
1,000 ,, concentrated nitric acid.

The pieces are passed for half an hour at 30 to 45° C. through this bath, washed thoroughly and soaped anew.

In the styles containing red, orange and white reserved under aniline black, Kopp operates as follows:—

After printing on the resist pass the goods through 10 litres of sulphate of soda solution, 400 grammes per litre, 150 grammes chalk, 300 grammes of sal ammoniac, diluted with the necessary quantity of water, rinse for half an hour and chrome for ten minutes at 66° C., in a bath containing 5 grammes of bichromate of potash per litre. Wash thoroughly and dye quickly in alizarine. Pass

through bran, chrome a second time as before, pass through a lukewarm bath of milk of lime to develop the orange, and finally soap.

Orange Resist I.

2 litres water,
4,000 grammes nitrate of lead,
1,800 „ acetate of soda,
4,250 „ dark British gum.

Orange Resist II.

$\frac{1}{2}$ litre water,
 $\frac{1}{2}$ „ acetate of lime, 20° B.,
1,000 grammes nitrate of lead,
450 „ dark British gum.

Red Resist.

2 litres aluminate of soda, 33° B.,
 $1\frac{1}{2}$ „ water,
1,000 grammes dark British gum.

White Resist.

1 litre acetate of lime, 20° B.,
800 grammes dark British gum.

When only the aluminate red resist and the white resist are printed on, the goods are passed through a bath containing, for the necessary quantity of water:—

1 litre water,
400 grammes silicate of soda, 10° B.,
1,000 „ sal ammoniac.

The passage lasts a minute and a half at 50° C. The pieces are washed for twenty minutes and dunged a second time at 50° C. in a bath containing 10 grammes of silicate per litre. The goods are then dyed as quickly as possible in alizarine, steamed and soaped.

Kielmayer recommends for the same style an orange containing basic nitrate of lead, with acetate of soda added in order to resist the black better:—

11,200 grammes nitrate of lead,
2,200 „ acetate of soda,
8 litres water,
4,200 grammes dark British gum.

Boil, and add when lukewarm:—

1,900 grammes caustic soda, 30° B.

The treatment for this is the same as that indicated for the orange and aniline black style.

In the white and coloured resists the various reducing agents

and neutralisers of which we have already spoken may be used, but these reserves are limited to aniline black printed on a single side of the cloth.

H. Koechlin (*B.S.P.* 1881, p. 286) describes a process allowing an aniline black dyed by C. Lauth's process to be operated upon. In this process, which we describe later, the black is dyed over manganese bistre. The discharges are printed over the bistre dyed cloth, and contain 400 to 500 grammes of tin salt per litre, in addition to the suitable colouring matters. On steaming, the bistre is destroyed at the places where the discharge is printed. The goods are padded through sulphate of aniline and the black is developed. By using alphanaphthylamine Koechlin obtained a garnet brown.

E. Kopp gives the following account of this process, which he formerly worked at Rouen. To obtain a good black it is indispensable to have a perfect bistre to begin with, and this he got with manganous chloride at 12° B. If the bistre is too dark, the black is brownish, and if the bistre is too light or if the aniline solution is too concentrated the black easily greens. The following are suitable discharges of manganese bistre:—

White.

8 litres thickening,
4,400 grammes tin salt,
2,200 „ hydrochloric acid.

Thickening.

3,000 grammes white starch,
3,000 „ flour,
12 litres water,
12 „ gum tragacanth jelly.

Blue.

1 litre white,
50 grammes tannin,
50 „ Methylene Blue.

Yellow.

750 grammes white starch,
250 „ British gum,
3 litres water,
1 „ Persian berry extract, 20° B.

Boil until this thickens, add when cold:—

$\frac{1}{2}$ litre Persian berry lake in paste,
3,700 grammes, 1 part tin salt dissolved in $\frac{1}{2}$ part hydrochloric acid.

Green.

- 6 litres thickening,
- 2,760 grammes tin salt,
- 2 litres tartaric acid, 30° B.,
- $\frac{1}{2}$ „ hydrochloric acid.

For each litre of colour, add:—

- 20 grammes Methyl Green,
- 5 „ tannin.

Thickening.

- 4,000 grammes white starch,
- 4,000 „ flour,
- 24 litres water.

Olive.

- 4 litres yellow,
- 1 „ blue.

Grey.

- 1 litre white,
- 1 „ Coupier's Blue solution, 100 grammes per litre,
- 200 grammes tannin.

Red.

- 4 litres white (freshly prepared),
- 1 „ primrose lake,
- $\frac{1}{2}$ „ curcumine lake,

Primrose Lake.

- 1,000 grammes stannate of soda dissolved in
- 25 litres boiling water.

Filter through a cloth, and dissolve in this:—

- 1,000 grammes Eosine.

Precipitate with 5 litres of sulphuric acid, 10° B., stir and filter without washing.

Curcumine Lake.

- 1,000 grammes stannate of soda,
- 12 litres boiling water.

Dissolve, filter, and add:—

- 4 litres cold water,
- $1\frac{1}{4}$ „ alcoholic solution of turmeric.

Stir for a few minutes, precipitate with:—

- 4 litres sulphuric acid, 10° B.

Wash by adding 48 litres water. Allow to settle. In this way 3,400 grammes of turmeric lake are obtained.

Cutch Brown.

12 litres	thickening for green,
5,000 grammes	tin salt,
1,500	„ hydrochloric acid,
2 litres	Persian berry extract, 30° B.,
$\frac{1}{2}$	„ logwood extract, 20° B.,
1	„ cochineal lake.

After dyeing, dry at moderate heat, expose for a night, then treat in the following manner:—If the pattern does not contain red, the goods are simply winched through a light chalk bath at 25° C., then washed in the continuous machine. Pieces containing red are passed in the same way through a bath at 25° C., containing 1,200 litres of water, 2,400 grammes acetate of lead, and 2,400 grammes acetic acid. The pieces pass from here into a small rinsing machine with spurt pipes. They are squeezed between a pair of rollers, rolled up at once with a dry back cloth, and dried on the cylinders.

These precautions are necessary to prevent the red from bleeding. The goods are then printed with the following black:—

30 litres	thin gum water,
8,400 grammes	aniline salt,
6,000	„ tartaric acid.

This colour is padded in the printing machine over the bistre already printed with the discharge colours. The goods are hung up for several hours, then winched through a bath containing 9 kilos. of alum in 3,000 litres of water. When seven pieces have been passed through, the bath has become too acid; for each of the following pieces, therefore, 600 grammes of acetate of soda are added. On leaving this bath the pieces are passed through the small rinsing machine, then submitted to the action of ammoniacal vapour in a continuous steamer, rolled up again in the dry back cloth and finally dried. The passage through ammonia vapour turns the black bluer and livens the red.

The passage through the alum bath lasts 30 seconds at a speed of 100 metres in three minutes. The passage through the ammonia vapour lasts two minutes at a speed of 100 metres in ten minutes.

H. Koechlin's process, consisting in padding goods first printed with tin salt discharges through a bath of aniline salt, has two principal disadvantages. In the first place, the padding bath becomes heavily charged with the tin salts, and secondly the brightness of the colours is affected by the bath. This is remedied by padding the aniline in the printing machine by means of two rollers closely pitted with dots, and giving the pieces a good nip in passing through this pair of rollers.

Kopp, Noelting and Grandmougin (*B.S.M.* 1894, p. 84) examined a process brought before the Mulhouse Society. In this method

the manganese bistre is not obtained in the ordinary manner with manganous chloride, but by precipitating permanganate of potash on the fibre by reduction with tannin. The cloth is tanned hot, and then passed through permanganate solution. The three reporters noted that the bistre thus obtained was less easy to discharge than that got with chloride of manganese. Moreover, good results could not be got by discharging the tannin, as in spite of this discharge enough bistre was produced to dirty the white. They reported therefore that the process had no advantage over that of H. Koechlin.

G. Witz in 1875 (*B.S.R.* 1874, p. 169) proposed to discharge the developed aniline black by printing on an acid solution of permanganate of potash, removing the black oxide by passing the goods through oxalic acid. It is difficult, if not impossible, to obtain a white by this process even at the cost of tendering the fibre.

H. Schmid (*B.S.M.* 1897, p. 411) obtains brown grounds by padding aniline black over developed paranitraniline red. The following is the bath for the aniline black, prepared in three separate solutions:—

2,800	grammes	aniline salt,
200	„	aniline oil,
12,500	„	water,
2,500	„	gum tragacanth water.

1,000	grammes	chlorate of soda,
12	litres	water.

1,800	grammes	yellow prussiate,
16	litres	water.

Mix before use, and bring the whole to 50 litres.

Red effects are got by printing acetate of soda over the padded black. If discharges capable of also destroying the paranitraniline red are used white effects can be obtained. The brown obtained by this process is extremely fast, but it is expensive and requires a very thorough soaping to free it from the peculiar odour resembling that of walnut husks.

PRUD'HOMME STYLES.

Maurice Phud'homme completely solved the problem of white and coloured effects on aniline black by taking advantage of Mather and Platt's rapid ager, which had then only recently been invented. Prud'homme commenced to produce these styles at Prochoroff's print works at Moscow, and described the process in a sealed document deposited with the Mulhouse Society in December, 1884. This was opened on July 13, 1887, but it does not go minutely into the details of the process.

O. Krafft and Buhning were the first to publish details. They give the following description:—

The thoroughly bleached cloth is rolled up and passed through the aniline black bath in a wooden trough with three wooden rollers. It is kept at full width by means of expanders, and on leaving the bath is squeezed by a pair of rollers, one of brass and the other coated with rubber, so that the excess of liquid runs back into the bath. These rollers can easily be mounted on the frame of a printing machine, and the nip must be regulated in the usual manner. Leaving these rollers, the cloth goes at once into a hot air chamber. The temperature of this has a considerable influence on the final result, and must be so regulated that the pieces leave it thoroughly dry. They are then of a light yellow, slightly greenish, colour. The attendant must take care that the run of the goods is continuous, and must connect the web ends without stopping the machine. If the colour is oxidised in the hot chamber and takes a pronounced green colour, it will not be possible to obtain a pure white. The pieces which turn green should not be used for patterns in which white is required. After drying, the pieces are rolled up as usual and printed with the discharges described later.

It is of first importance that the goods should be thoroughly dried in the hot chamber after printing. They are then passed once or twice, according to the temperature and speed, through the Mather and Platt, so that they turn a beautiful dark green. They are then chromed at full width at 80° C. in a bath containing, per litre, 10 grammes of bichromate of potash, 5 grammes of ammonia soda, and 5 grammes of rough salt. They are washed, soaped, rinsed and finished. The aniline bath is prepared as follows:—

1,500	grammes	chlorate of potash, dissolved in
40,000	„	water. Add
4,000	„	yellow prussiate solution, 28:100,
2,600	„	aniline salt,
<i>x</i>	„	aniline oil.

The aniline salt should be neutral, the *x* quantity of aniline oil to be added is calculated according to the state of the aniline salt used.

White Discharge.

10,000	grammes	British gum,
6,000	„	water,
16,000	„	acetate of lime, 16° B.

Boil, and add cold:—

5,000	grammes	acetate of soda,
5,000	„	caustic soda, 20° B.

Yellow Discharge.

10,000	grammes	chrome yellow	paste
6,000	„	albumen	water
2,000	„	acetate of soda	
600	„	caustic soda,	20° B.

Red Discharge.

16,000	grammes	vermilion	
22,000	„	glycerine	
2,000	„	water	
2,000	„	acetate of soda	
8,000	„	albumen	water.

Blue Discharge.

7,000	grammes	ultramarine	
14,000	„	albumen	water
2,000	„	acetate of soda.	

The recipes and method of working given by Krafft and Buhring for the Prud'homme style are still in current use.

Lauber (*F.Z.*, 1897, p. 65 and 104) proposed to replace the chlorate of potash in the aniline bath as above by chlorate of soda, which is much more soluble.

Kertesz (*F.Z.*, 1890) uses ferrocyanide of ammonia and gives the following recipe :

3,500	grammes	chlorate of soda,	dissolved in
20	litres	water	
5,500	grammes	aniline oil,	dissolved in
6,250	„	hydrochloric acid,	19½° B.
10	litres	water	

Mix and add after cooling

12 litres ferrocyanide of ammonium.

Bring up to 63 litres by adding water.

The goods are padded in this bath, and dried either on the stenter or by hanging. The use of this bath facilitates the discharge, inasmuch as the padded cloth has less tendency to oxidise as rapidly as that prepared according to Prud'homme's recipe.

The drying may even be done on the drying cylinders covered with cloth. Another advantage is that the pieces may be kept 24 hours before completing the process. After drying, an alkaline discharge is printed on, dried, and steamed in a single passage through the Mather and Platt. The goods are not chromed; they are washed, first at 50° C., then a second time at 30° C., and finished as usual.

In current practice, however, ferrocyanide of potassium is substituted for the ammonium salt on account of the difference of cost. The three roller padding machine should be used and provided with a wooden trough. The longer the bath the better the impregnation of the goods, and the black is fuller without being any more

difficult to discharge. The dimension of the trough, however, is naturally limited by the tendency of the aniline to oxidise; the use of a standing bath cannot be recommended, and if a considerable quantity of dyebath has to be run off and wasted each day, the cost of production is increased too considerably.

As a rule, the trough should hold from 50 to 70 litres. The pressure is regulated so that the fibre takes up 90 to 100 per cent. of its own weight.

This padding bath is prepared in two solutions, which are mixed immediately before use. The first contains the salt of aniline and the chlorate, and the other contains the prussiate. Another way is to dissolve the aniline salt with the prussiate and add a solution containing the chlorate alone. The tone of the black may be modified either by varying the strength of the aniline bath, by the addition of toluidine, or by regulating the strength and temperature of the subsequent chrome bath.

Mercerised cotton takes a much stronger and fuller black than unmercerised goods. The bath may be 20 to 30 per cent. weaker than for non-mercerised cotton, and better results may nevertheless be obtained. The limpidity of the bath has also an effect upon the quality of the black.

Lauber (*F.Z.*, 1897, p. 64) notes that the padded pieces may be dried without danger at 50 to 60° C. This may be done on the stenter or over the cylinders. The drying stenter should be arranged so that the steam pipes are placed on the exterior, in order to dry by hot air alone, as very hot places in the interior of the stenter produce heat rays that interfere with the uniformity of the shade. Still another precaution is taken to avoid this fault; the pipes are wrapped in poor conductors of heat, for instance old back cloths.

Drying over the drums is the usual practice in England and in America, and in works where there are no drying runs or stenters, or again, where it is necessary to avoid fold marks, which often form in the hot chamber in the case of goods with woven patterns, particularly with those striped lengthways. Drying over the cylinders requires great care and they should be clothed.

Lauber recommends that the padding bath should contain per litre 30 to 40 grammes of chlorate of soda, 55 to 67 grammes of prussiate of potash, and 80 to 90 grammes of aniline salt. He gives the following example:—

5,400 grammes chlorate of soda
58 litres water.

10,800 grammes yellow prussiate
58 litres water.

16,800 grammes aniline salt
58 litres water.

Equal parts of these three solutions are mixed immediately before use. In this case the bath contains 31 grammes of chlorate, 65 grammes of prussiate, and 97 grammes of aniline salt per litre.

Lauber also gives another recipe :—

2,380 grammes chlorate of soda,
15 litres of water.

3,300 grammes yellow prussiate,
15 litres of water.

Mix and add

6,100 grammes aniline salt dissolved in water,
840 „ aniline oil.

Bring the whole to 80 litres.

This black contains about 76 grammes of aniline salt, 10½ grammes of aniline oil, 41 grammes of prussiate, and 30 grammes of chlorate of soda per litre.

The following black has been adopted in practice for the Prud'homme style :—

79 grammes aniline salt,
8 „ aniline oil,
30 „ chlorate of soda.

Dissolve in water, bring up to 500 c.c. and add immediately before use 44 grammes of yellow prussiate dissolved in sufficient water to give 500 c.c.

Since it was first introduced the Prud'homme style has been greatly improved, both in the perfection of the discharge effects and as regards variety of application. It must be noted here that we call by the name of “discharges” the colours printed over undeveloped padded black. This terminology is not quite correct, but it differentiates this class of colour from oxide of zinc colours, which we describe later under their correct name of “reserves” or “resists.”

A good result in discharge styles depends on many conditions. The chief requirement is that the black ground shall be full and strong in order to obtain the necessary contrast. We have already said that the bath must be exactly prepared, and that a thorough bleach is indispensable, especially for mercerised goods.

The discharges must be printed on before oxidation. To ensure this a fresh bath is used, the pieces are dried carefully at not too high a temperature, they are cooled after leaving the drying machine, and then printed as quickly as possible. In order to get a full and beautiful black too extreme drying must be avoided, and there must be no rest in the process after printing on the discharges. There should be no more rollers in the continuous drying machine than are strictly necessary to dry the discharges completely, but without carrying the drying process too far.

The goods are always developed in the Mather and Platt. They are passed through once or twice for one or two minutes at a temperature of 95° C. The condition of the steam has a great effect on the result; if it is too moist the white has a yellow tinge. If the Mather and Platt has been at rest for some time one or two greys should be passed through to absorb the moisture arising from the condensation of the steam.

Frequent change of atmosphere, suggested by C. Brandt, gives good results, but it is too expensive.

Caustic soda was used at first in white discharges, but its use has been given up on account of the tendency of strongly alkaline printing colours to bleed. Commercial sulphite of potassium, recommended by Meister, Lucius and Bruning for colour resists under paranitraniline, seems to be more suitable. The high price of this salt as compared with that of caustic soda is compensated by the fact that a cheap starch thickening may be used with it. Sulphite of potassium alone, or with the addition of acetate of soda, gives very good whites, and is specially suitable for mourning styles. Kertesz gives the following recipe:—

3,000	grammes	acetate of soda,
500	„	ammonia soda dissolved in
5,000	„	thick starch paste, add after cooling,
250	„	bisulphite of soda, 38° B.

If this colour becomes too thin on standing for some time it is thickened with gum arabic powder.

Kertesz says that the washing should preferably be done with washing machines with little or no pressure on the rollers. A pure white is obtained in this way, otherwise the black, which always bleeds a little in the first washing, is rubbed on to the white by the pressure of the rollers.

The following white has long been used:—

2,380	grammes	British gum,
1,430	c.c.	water,
3,810	grammes	acetate of lime, 16° B.,
1,190	„	acetate of soda crystals,
1,190	„	soda caustic, 20° B.

Lauber recommends also the following formula:—

1,250	grammes	white starch,
4,150	c.c.	water,
2,550	grammes	gum tragacanth jelly, 50 per 1,000,
750	c.c.	acetic acid, 6° B.,
2,350	grammes	acetate of soda crystals,

Boil and add when cold,

1,200	c.c.	acetate of lime 15° B.,
1,200	„	bisulphite of soda, 15° B.,

Prud'homme's white discharge is made with :—

2,000	grammes	dark British gum,
4	litres	water,
750	grammes	acetate of soda,
500	..	caustic soda, 20° B.,
250	..	bisulphite of soda, 36° B.

The acetate of soda can advantageously be replaced by the sulphite. The following white is also used :—

300	grammes	sulphite of potassium,
150	..	acetate of soda,
2	..	ultramarine,
550	..	starch thickening.

The effect of the white discharges is very much improved by the addition of white mineral pigments to the discharge paste.

These should penetrate into the pores of the cloth and be fixed in this manner. The pigment gives a smooth surface and a better white. The proportion of the mineral colour must not be so heavy as to hide the fibre completely; in this case the colour will be difficult to print and the white will adhere to the drying cylinders. The minerals used are zinc white, sulphate of barium, or lithopone, which are applied without any special thickening agents, unless it is considered desirable to add a small quantity of pure gelatine.

For colour discharges the pigments can be brightened with aniline colours and a number of coal tar colours have been used as pigments in the state of tannin or zinc lakes.

For use as discharges soda or citrate of soda is added to the colour pigment. The aniline colours fixed with albumen are mixed with acetate of soda, the following recipes have proved successful :—

Yellow.

200	grammes	neutral tragacanth jelly, 50 per 1,000,
250	..	albumen solution, 50 per cent.,
40	..	ammonia soda,
120	..	citrate of soda, 28° B.,
40	..	turpentine,
350	..	dry chrome yellow,
10	..	Thioflavine T.

Red.

150	grammes	tragacanth jelly,
220	..	vermilion,
20	..	Rhodamine B.,
250	..	albumen solution,
70	..	ammonia soda,
30	..	turpentine,
260	..	water.

Blue.

150	grammes	tragacanth jelly,
350	„	ultramarine,
300	„	albumen solution,
70	„	ammonia soda,
10	„	ammonia,
20	„	turpentine,
100	„	water.

For the colour discharges with the artificial colouring matters the thickening is tragacanth and albumen, to which is added, according to the intensity of the black and the depth of the lines of the engraving, from 250 to 300 grammes of acetate of soda per litre. The most suitable colouring matters are Rhodamine 6 G, Irisamine, Auramine, Thioflavine, Brilliant Green, Methylene Blue, New Methylene Blue, Saffranine T, M, and N. These are used either in the form of lakes or in simple solution, and are fixed by the albumen in the thickening. The lakes are the faster to light. The addition of metallic salts which will not coagulate the albumen increases the vivacity of the discharge colours.

The goods after leaving the Mather and Platt are chromed, well rinsed and lightly soaped. The chrome bath is used cold, or at about 40 to 50° C. In the latter case the black is somewhat redder. About 5 to 10 grammes of bichromate of potash per litre is used, and the free chromic acid is often neutralised by the addition of chalk. The darker the aniline black on leaving the Mather and Platt, the less chromate is used. If the bath does not contain sufficient aniline a rather thin green is obtained on steaming. This can be improved to some extent by increasing the proportion of bichromate up to 12 grammes per litre.

The mourning style, black alone on white, is washed in rope form after chroming, and it is better not to soap the goods.

The Prud'homme style will stand a mild soaping at full width, but it is frequently sufficient to wash it at full width or in rope form.

When the discharge is dyed red, with or without white in the pattern, the goods, of course, are not chromed. In place of the bichromate the bath contains 10 to 20 grammes per litre of sal ammoniac and soda, keeping it slightly alkaline.

Colour discharges in the Prud'homme style were obtained with the colours fixed by albumen to begin with. This is an expensive method, and the endeavour was made to introduce more transparent colours, and at the same time to make it easier to raise the goods after printing.

Direct cotton colours printed with caustic soda, or soda, were proposed. Among others, Diamine Pure Blue, Oriole Yellow, and Cotton Yellow were used. Steiner (*B.S.M.*, 1897, p. 137) recommended Rosophenine. The colours thus obtained were lacking in brightness, and were not very fast to washing.

Blue.

400	grammes	starch thickening,
200	„	tragacanth jelly.
25	„	Diamine Pure Blue,
100	„	ammonia soda,
40	„	caustic soda, 20° B.,
245	„	water.

Grafton and Browning (*E.P.*, 11,416, 1892) use basic colours fixed with tannin. The goods are passed through two consecutive baths of tannin and tartar emetic, washed, dried, and padded in the aniline black bath, which is slightly acidulated in order to decrease

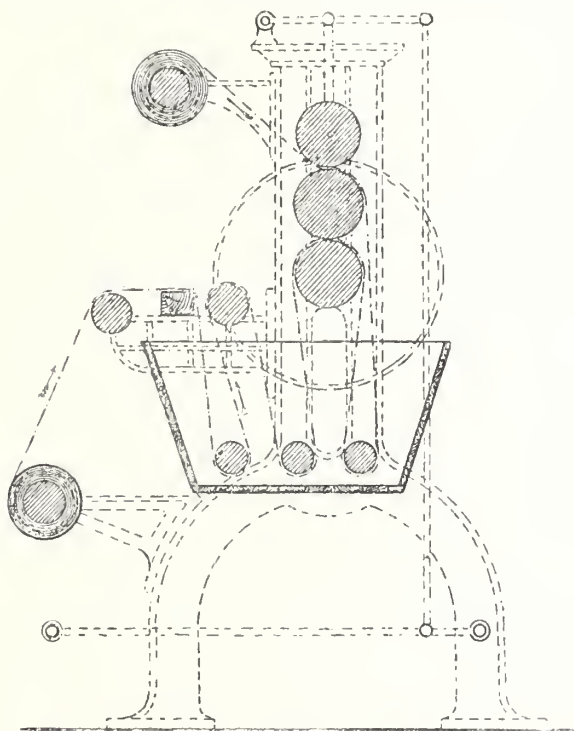


FIG. 1.—THREE-ROLLER PADDING MACHINE.

the reducing properties of the tannin. The discharge colours contain acetate of soda, and the basic colouring matters, which are fixed by the tannate of antimony during the passage through the Mather and Platt.

E. P. Pearson (*A.P.*, 491,961, 1893) pads in the usual aniline black bath; prints on a resist made with the colour and tannin alone, then passes the goods through the Mather and Platt, and finally through a bath of an emetic.

C. Donald (*A.P.*, 491,951, 1893) adds either the tannin or the emetic to the padding bath, thus sparing one of the steps of the Grafton process.

Grafton and Browning's process gives the best results. At the same time it will be noted that two supplementary operations are required, and this makes C. Donald's process frequently preferable. The goods are padded through tannin, and the antimony is added to the padding bath and the colour.

Caberti and Peco (*F.Z.*, 1895, p. 346) recommend "antimony salt" in preference as the addition to the padding bath. The discharges are more delicate than those fixed with albumen, but they are less bright, in consequence, to some extent, of the action of the tannin on the iron of the prussiate.

Schmid (*C.Z.*, 1902, p. 271) states that when tannin is used in excess it resists the aniline black, and if it is used in insufficient quantity the fastness of the basic colours is decreased.

PRUD'HOMME STYLES ON FLANNELETTE.

Grafton's process is especially suitable for the superior class of flannelette known as molleton, called by the French *veloutine*. In these goods the brightness of the colour is less important than its capacity to penetrate the material as completely as possible. Both sides of the cloth should look alike and complete penetration of the colour also renders the raising operation easier.

R. Weiss (*R.G.M.C.*, 1899, p. 243) gives the following description of the manufacture of molleton at Kingersheim, near Mulhouse.

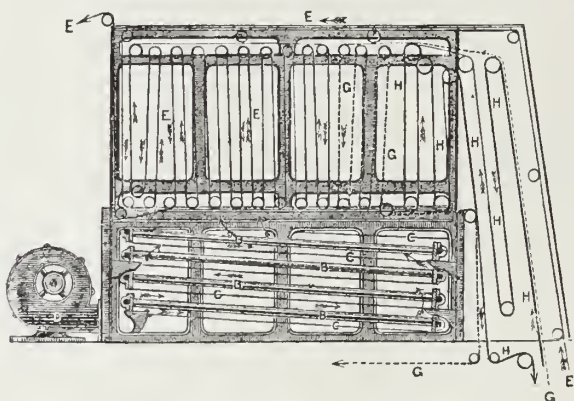


FIG. 2.—HOT AIR DRYING MACHINE.

The grey pieces are malted at a temperature not higher than 65° C., washed and dried. Thus freed from size, they are padded twice through an aniline black bath in a three-roller padding machine.

Fig. 1 is taken from "The Dyeing of Cotton Fabrics," by Franklin Beech, by permission of Messrs. Scott, Greenwood, and Co. This type of padding machine has a fixed intermediate roller. The upper and lower rollers have each a system of levers and counter-weights, so that the nip of each on the middle roller can be regulated independently, and each has a lever with a cam action that allows either to be thrown instantaneously out of play with the middle roller.

The cloth is guided through the liquor and twice through the squeezing rollers. The first nip impregnates the fibre before it again passes through the bath, and the second nip makes the dyeing more complete and even, and at the same time a stronger nip is given in order to squeeze out as much liquor as possible and thus commence the drying action.

This padding machine is arranged to work continuously with a hot air drying machine. In the type shown, the fan D forces a current of air in a zig-zag course through the channels C surrounding the steam-pipes B. The heated air passes into the upper chamber and flows in a contrary direction to the run of the pieces, making its exit at the top. On leaving the machine the pieces are cooled and printed the same day, as far as possible, with the reserve colours.

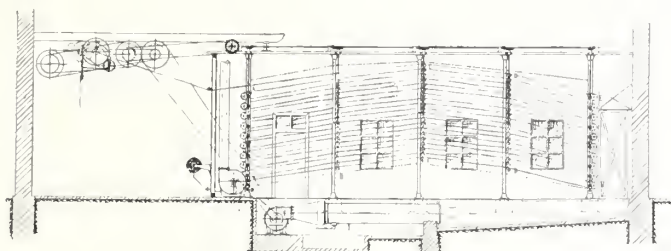


FIG. 3.—HOT AIR DRYING MACHINE.

Fig. 3 is the special hot air drying machine, or "hot flue," manufactured by the Zittauer Maschinenfabrik, of Zittau i/S, Germany.

The engraving of the printing rollers should be deep and the colours thin, in order to get sufficient penetration. The goods are steamed for five minutes in the Mather and Platt, chromed, washed and dyed. From 2 to 5 passages are then given in the raising machine on each side of the cloth.

Bath for Aniline Black.

6,000	grammes	chlorate of soda,
10,000	„	yellow prussiate,
16,000	„	aniline salt,
4,000	„	liquid tannin,
8	litres	gum tragacanth water.

Bring up to 200 litres with water.

White.

5,000	grammes	British gum,
7	litres	sulphite of potassium,
5	„	water.

Cream.

700	grammes	Phosphine,
5,000	„	British gum,
6	litres	acetic acid,
7	„	sulphite of potassium.

ANILINE BLACK.

Golden Yellow.

1,000	grammes	Auramine II.,
5,000	„	British gum,
3	litres	acetic acid,
2	„	water,
7	„	sulphite of potassium.

Green.

1,000	grammes	Auramine II.,
150	„	Methylene Blue,
5,000	„	British gum,
3	litres	water,
3	„	acetic acid,
7	„	sulphite of potassium.

Blue.

500	grammes	Methylene Blue,
5,000	„	British gum,
3	litres	water,
3	„	acetic acid,
7	„	sulphite of potassium.

Violet.

300	grammes	Methylene Violet,
80	„	Methylene Blue,
5,000	„	British gum,
3	litres	water,
3	„	acetic acid,
7	„	sulphite of potassium.

Red.

500	grammes	Safranine,
150	„	Auramine II.,
300	„	Rhodamine, 6 G,
5,000	„	British gum,
3	litres	acetic acid,
3	„	water,
7	„	sulphite of potassium.

Orange.

700	grammes	Phosphine,
50	„	Auramine,
80	„	Safranine,
6,000	„	British gum,
4	litres	acetic acid,
5	„	water,
9	„	sulphite of potassium.

Grey.

2,000 grammes	Grey 4 B (Poirrier),
3,000 ,,	hydrate of zinc,
3,100 ,,	British gum,
3 litres	water.

To each of these colours, with the exception of the grey and the white, 100 c.c. per litre of a saturated solution of emetic and common salt is added.

The malted pieces may be padded through a bath of 8 to 10 grammes per litre of tannin, dried and padded twice through a bath for black containing 20 grammes per litre of antimony salt. Another method is to pad twice through an ordinary bath for black without addition of antimony salt, but with rather less aniline than usual, and then to print on a colour containing soda emetic.

400 grammes	British gum,
360 ,,	sulphite of potash,
28 ,,	Methylene Blue,
20 ,,	sodium tartar emetic,
100 ,,	acetic acid,
92 litres	water.

The use of sodium tartar emetic has been suggested by Meister, Lucius and Bruning.

Oswald's ferrocyanide of zinc reserves, described later, are also suitable for molleton.

Some other processes of discharging padded aniline black may be pointed out. Bloch and Schwartz (*B.S.M.*, 1896, p. 301) use sulphocyanide of tin to coagulate the albumen. The sulphocyanide of tin discharge is printed to begin with on the goods padded through the bath for black, and an albumen colour containing acetate of soda is then printed over. In all the places where the sulphocyanide of tin comes in contact with the albumen this is coagulated to the surface of the tissues, and is taken off in washing. Coloured effects are obtained by adding basic colours to the white discharge. Tannin and emetic in solution in chloride of lime are added to the printing colour to fix the basic colours, and according to Jeanmaire this produces tannate of antimony on steaming. Bloch and Schwartz use the following printing colours:—

White Discharge I.

2,100 grammes	sulphocyanide of barium.
2,175 litres	water,
1,750 grammes	tin salt,
4,000 ,,	British gum.

White Discharge II.

3,500	grammes	tin salt,
2,800	,,	sulphocyanide of potassium,
7,500	,,	water,
8,000	,,	British gum,
1,000	,,	wheat starch,
500	,,	water,
2,500	,,	sulphate of zinc,

Colour Discharges.

2,100	grammes	sulphocyanide of barium,
1,000	,,	water,
1,750	,,	tin salt,
2,500	,,	solution of the colour,
4,000	,,	British gum.

Add when cold:—

5,000	grammes	tannin,
300	,,	acetic acid, 6° B.,
250	,,	emetic solution.

Solution of the Colour.

50	grammes	dye stuff,
500	,,	water,
500	,,	acetic acid.

Solution of Emetic.

140	grammes	emetic,
1,000	,,	chloride of lime solution, 8° B.

Bloch and Schwartz consider the white discharge II. to be the better; the sulphate of zinc assists to coagulate the albumen. Romann does not consider sulphocyanide of tin to be a good white discharge. Caberti uses sulphocyanide of tin for colour discharges, combining it for this purpose with the Eosines, Cotton Yellow 2 B (Geigy) Thioflavine T, or New Methylene Blue N, fixed by adding acetate of chrome to the colour. This style is not very fast to washing.

A. Scheurer (*B.S.M.*, 1900, p. 138) fixes the basic colours by means of tungstic acid. The goods are padded through tungstate of soda, then passed through sulphuric acid. They are washed, dried, padded through aniline black, and the discharge colours containing basic colouring matters and acetate of soda are printed on. The goods are then steamed two minutes, washed and chromed. In addition to acting as a mordant for the basic colours, the tungstic acid aids the development of the black, whereas tannin has the opposite effect. The lakes are fixed by the steaming; they will stand soaping for half an hour at 60° C., but are washed out at 80° C.

S. Wallach, C. Schoen, and H. Bourry, replace the albumen in the colour discharges by gelatine or casein, to which they add an

easily dissociated compound of formaldehyde, capable of setting formol at liberty on steaming. The formol renders the gelatine or the casein insoluble. Ammoniacal compounds of formaldehyde are used in the proportion of 4 per cent. of the weight of the gelatine. The following recipes have been used for this process :—

Blue Discharge.

10 litres	thickening G,
4,000 grammes	ultramarine,
400 ,,	ammoniacal solution of formaldehyde,
350 ,,	carbonate of soda.

Thickening G.

32 litres	solution of gelatine,
32 ,,	tragacanth gum water,
12,000 grammes	acetate of soda.

Solution of Gelatine.

3,000 grammes	gelatine,
1 litre	water.

Ammoniacal Solution of Formaldehyde.

1,000 grammes	formaldehyde, 40 per cent.,
1,250 ,,	ammonia.

Yellow Discharge.

6,000 grammes	chrome yellow lake,
11 litres	thickening G.,
400 grammes	ammoniacal solution of formaldehyde,
350 ,,	carbonate of soda.

Pink Discharge.

11 litres	thickening G.,
4,000 grammes	pink lake (Thann and Mulhouse),
400 grammes	ammoniacal solution of formaldehyde,
350 ,,	carbonate of soda.

Green Discharge.

9,000 grammes	green lake (Thann and Mulhouse),
11 litres	thickening G.,
400 grammes	ammoniacal solution of formaldehyde,
350 ,,	carbonate of soda.

W. Popielsky (*F.Z.*, 1900, p. 39) has endeavoured to obtain discharge effects by printing on the nitrate, which transforms the aniline into diazo derivative, and thus prevents the oxidation of the black.

A Scheurer (*B.S.M.*, 1900, p. 139) says that tungstate of soda is sufficiently alkaline to discharge the aniline black. A colour is printed on containing 200 grammes of tungstate of soda per litre. If pigments are added to this and tungstate of barium is precipi-

tated on the fibre by a passage through chloride of barium these colours are fixed. This process allows opaline effects to be produced over aniline black.

F. Binder and Frossard (*B.S.M.*, June, 1902) obtain semi-resists under prussiate black by using citrate of tin and soda. By adding sulphate of iron to the resist Prussian blue is formed, and the grey is more beautiful.

F. Binder and C. Sunder (*B.S.M.*, 1901, p. 330) fix the colour discharges by replacing the albumen by gelatine. They noted that the gelatine could be coagulated by steaming for an hour when 4 per cent. of its weight of carbonate of soda, or 5 per cent. of its weight of acetate of soda is added. A number of other salts may be used for the same purpose. The best results have been obtained with acetate of zinc, with which colours may be prepared, which keep well in a cold place. With this salt the gelatine is completely coagulated by a passage of four minutes in the Mather and Platt.

Binder and Sunder prepare their discharge with a 25 per cent. solution formed by boiling together for six hours equal parts of dry gelatine and gum tragacanth jelly, 10 per cent. of acetate of zinc crystals, 15 per cent. of acetate of soda crystals, and 20 per cent. of oleine.

L. Baumann (*B.S.M.*, 1901, p. 329) obtains very bright effects over aniline black by this process. The lakes are not quite so fast as when albumen is used, but the cost of production is much less.

Cheap dark shades of indigo can be obtained with the aid of aniline black. A bottom of blue is given by two dips in the vat, then the goods are padded through an ordinary bath for black reduced to a third or a quarter of its concentration by the addition of water. For this style acetate of soda is added to the coloured bichromate discharges. For the white an excess of caustic soda is used.

White.

140 grammes	bichromate of soda.
120 ,,	caustic soda, 40° B.,
740 ,,	British gum water.

Yellow.

300 grammes	chrome yellow, in powder.
250 ,,	egg albumen solution, 50 per cent.
90 ,,	bichromate of soda neutralised with ammonia,
120 ,,	acetate of soda,
80 ,,	gum tragacanth water.

The black is oxidised to begin with in the Mather and Platt, then the indigo is discharged by a passage through a mixture of sulphuric and oxalic acid.

The Prud'homme style at first seemed very difficult to work, but it is now an every day article. The very nature of the process

allows us to understand its early want of success. The padded goods must be passed twice through the hot chamber, first when they leave the padding bath, and secondly after the discharges have been printed on, and the green must not be developed during either of these dryings under penalty of spoiling the beauty of the black or the brightness of the discharge colours. Moreover, to avoid the greening produced by a prolonged ageing, the padded goods must be printed the same day. These reasons make it indispensable that the work should be methodically organised, and in order to avoid limiting the output it is very often necessary to work over-time.

OXIDE OF ZINC RESISTS.

A variation of the Prud'homme process has been realised by printing the goods with an oxide of zinc resist, which allows them to be padded at any convenient time in the aniline black bath. This process permits the work to be more easily arranged and largely increases the output. The padding process may be the ordinary one, or a special method.

We give here a short history of the zinc resist which led up to the oxide of zinc resist actually in use.

C. Reber and H. Schmid (*B.S.R.*, 1884, p. 758) pointed out in 1884 that ferrocyanide of zinc possessed the property of giving insoluble lakes with the basic colouring matters.

The Thornliebank Co., Ltd., and W. E. Kay (*E.P.*, 713, 1893) patented the use of acetate of zinc as a discharge over aniline black, and at the same time as a fixing agent for the basic colours. The specification also indicated the possibility of interchanging the order of the padding and of the printing, and of using, for instance, acetate of zinc under the ordinary conditions of the Prud'homme process.

W. P. Whitehead (*E.P.*, 1,351, 1893) patented the use of oxide of zinc as resist. Used alone it gives a white, and for colour resists the basic colours are added without the special mordant for these colours. According to his specification, the oxide of zinc resist can be printed on before, or after, padding the goods.

Dreyfus (*J.S.C.I.*, 1894, p. 485) communicated a letter from J. Riley to the Manchester section of the Society of Chemical Industry, which stated that the Thornliebank Company, of Glasgow, had used oxide of zinc as a resist before padding with aniline black as early as May, 1880. The oxide of zinc was merely intended to resist the black, and not to fix the basic colours containing tannin which were used in the colour resists. The pieces printed with the oxide of zinc resist were steamed for an hour before padding.

C. Schoen sent to the Mulhouse Society on March 14th, 1894, some specimens of aniline black with coloured discharges, in which the basic colouring matter in the discharge paste was fixed without tannin by transformation into ferrocyanide of zinc lake. These colours resisted soaping at 40° C.

F. Oswald (*B.S.M.* 1894, p. 264) communicated a process that he had used in Russia. In this method he fixed the basic colours in the state of ferrocyanide of zinc lakes over the aniline black bottom. As a resist he used acetate of magnesia. The following is a specimen recipe:—

500 grammes acetate of magnesia, 20° B.,
400 „ British gum.

Boil, and add when cold:—

15 grammes Methylene Blue,
100 „ acetic acid,
60 „ sulphate of zinc.

The colours which are best for this style are Magenta, Safranine, Auramine, Thioflavine, Malachite Green, and Rhodamine. Very bright colours are obtained, but the lakes are not very fast to soaping, and have still less resistance to light. The following are two recipes used in the Oswald process:—

Light Blue.

520 grammes British gum paste,
5 „ Thionine Blue O (M.L. and B.),
25 „ acetic acid,
250 „ acetate of magnesia, 20° B.,
50 „ sulphate of zinc,
150 „ acetate of soda crystals.

Yellow.

500 grammes British gum paste,
20 „ Thioflavine T,
30 „ acetic acid,
250 „ acetate of magnesia, 20° B.,
50 „ sulphate of zinc,
150 „ acetate of soda crystals.

Caberti, Roggieri and Barzaghi (*R.G.M.C.* 1906, p. 164) who had had much experience in resist styles on flannelette, tried Oswald's method and found the results a little lacking. They state that resorcin and hydro-sulphite give better effects.

White Resist.

1,000 grammes Hyraldite W,
1,000 c.c. gum tragacanth 1:20.

Yellow Resist

35 grammes Thioflavine T,
5 „ Acridine Orange NO,
250 c.c. British gum 1:1,
100 „ water,
50 „ glycerine.

Boil until the dye-stuff is dissolved, then add:—

500 c.c. White Reserve,
100 „ alcoholic solution of resorcin.

Other colours are prepared in a similar way.

Schweitzer and Dickerson (*A.P.* 539,550, 1895) use oxide of zinc as a resist under aniline black in combination with betanaphthol and Nitrosamine to give a red. This process has no practical value.

Oxide of zinc as a resist colour printed on before padding with aniline black was first used in Great Britain and in Russia. It was noted that the pieces thus printed and padded required to be dried over the cylinders in order to prevent the resist from running. Oxide of zinc resists must be printed on thoroughly bleached and well brushed calico. The engravings should be rather deeper than for the ordinary Prud'homme styles, and a good quality of brush should be used as furnisher. The pieces are dried thoroughly, and remain rolled up until they are padded with the aniline black bath. It is not necessary to steam unless the resist contains albumen colours, and in this case a passage of two minutes through the Mather and Platt is sufficient.

The best method of padding is to use the two roller machine, shown in Fig. 4. This is arranged so that the goods do not go through the bath itself, but are guided between two rollers, with the side printed with the reserve pressing against the lower roller. This is of much larger diameter than the upper roller, and turns in the bath. It is either clothed or engraved with fine dots. In order to get sufficient colour on the goods, they are guided by the roller *i*, which keeps them in touch for a few inches with the roller running in the bath.

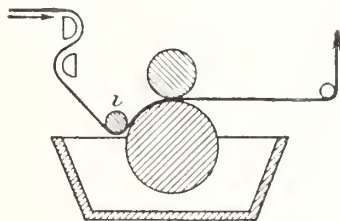


FIG. 4.—PADDING OUTSIDE THE BATH.

The padding liquor is slightly thickened with neutral gum tragacanth water, and the level in the colour trough is kept constant. The penetration is regulated by the pressure of the upper roller, which is covered with indiarubber.

On leaving the padding machine, the pieces run directly over the cylinders and are well dried; the colour must not be allowed to form, but the cloth must be hot on leaving the drums. The black is then developed as usual by a passage of two minutes through the Mather and Platt. The goods are chromed at 30° C., with 5 grammes of bichromate of soda and 5 grammes of chalk per litre, and washed at full width.

Padding Bath.

75	grammes	aniline salt,
8	..	aniline oil,
50	..	yellow prussiate of potash,
40	..	chlorate of soda,
50	..	gum tragacanth water.

Bring up to one litre.

Pink Resist.

200	grammes	oxide of zinc,
100	..	water,
492	..	light British gum paste,
40	..	turpentine,
20	..	glycerine,
48	..	Rhodamine 6 G,
100	..	water.

Yellow Resist.

200	grammes	oxide of zinc,
100	..	water,
510	..	light British gum paste,
40	..	turpentine,
20	..	glycerine,
30	..	Auramine O,
100	..	water.

Straw Colour Resist.

200	grammes	oxide of zinc,
100	..	water,
510	..	light British gum,
40	..	turpentine,
20	..	glycerine,
10	..	Thioflavine T,
120	..	water.

Red Resist.

200	grammes	oxide of zinc,
100	..	water,
400	..	light British gum paste,
40	..	turpentine,
20	..	glycerine,
30	..	Rhodamine 6G,
10	..	Safranine P,
10	..	Auramine,
59	..	acetine,
100	..	egg albumen, 50:100,
30	..	citrate of soda.

Blue Resist.

200	grammes	oxide of zinc.
100	..	water,
480	..	light British gum paste,
40	..	turpentine.
20	..	glycerine.
10	..	Thionine Blue O,
120	..	water,
20	..	bisulphite of soda.

The printing colours should be carefully ground before use. The oxide of zinc is made into a paste with the water, glycerine and turpentine, the thickening is added, and the whole is ground for twenty-four hours in a colour mill. The solution of the colouring matter or the colour lake is then added to the homogeneous paste. The slight addition of bisulphite increases the brightness of the ferrocyanide of zinc lakes.

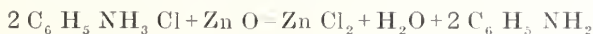
Egg albumen should be added in order to ensure complete fixation, but this addition is made immediately before printing. When oxide of zinc colours contain albumen, they have an unfortunate tendency to clog the engraving. Possibly this may be remedied by replacing the albumen by gelatine, as in the Binder process.

Colours faster to light are obtained by using tannin or ferrocyanide of zinc colour lakes instead of the dyestuff solutions. These lakes are put on the market by the Fabriques des Produits Chimiques of Mulhouse, by Wacker and Schmitt of the same town. Bloesch of Moscow, Fischer and Hunold of Milan, and by others. These lakes have merely to be added to the thickening. Whether the solution or the lake is used, a good penetration is obtained, and the design shows well on the back of the cloth. This is the reason that the resist process is preferable, and especially suitable for handkerchief printing and for flannelette.

As a white resist, oxide of zinc can be used alone, but it is better to add precipitated chalk; and the resist effect is improved by adding caustic soda, but not in sufficient quantity to make the printed reserve run on padding.

Oxide of zinc resists give very brilliant effects, but as we have said are insufficiently fast to light and washing. They are specially suitable for heavy designs, after the manner of those preferred in Eastern markets. Fine patterns cannot be produced with sufficient clearness.

H. Schmid (*C.Z.* 1902, p. 272) explains the part played by oxide of zinc in resist colours by the following equation:—



The aniline is thus extracted by oxidation, the chloride of zinc gives ferrocyanide of zinc by double decomposition with the yellow

prussiate, and this precipitates the basic colouring matters as insoluble lakes.

Drying over the cylinders is, as we have already said, indispensable to the success of the process. As compared with drying in the hot air chamber, it has the advantage of largely increasing the output; one padding machine working with a range of cylinders can easily follow three or even four printing machines. Too extreme a drying must be avoided; if the pieces have turned green when they leave the drums, a fine black will not be obtained.

The first drying cylinders are wrapped in cotton cloth or given less steam than the following ones, in order to avoid too prompt a drying. When the operation is properly conducted, the pieces have a yellow tint when they leave the drums.

W. Pluzanski has experimented with insoluble azo colours formed on the fibre under Prud'homme's aniline black. His process, deposited under seal with the Mulhouse Society on March 16, 1897, was examined by H. Schmid, who made the following report on December 4, 1907:—

“This problem is not easy to solve, as the azo colours must be given a resistant basic character and the naphtholate of soda must be eliminated from the fibre before padding with aniline black. To fulfil these conditions, Pluzanski added acetate of zinc to the diazo printing paste for red, or used directly the double zinc salts of the diazos for claret. After printing and coupling the diazo with the naphthol already padded on the cloth, he passed the goods through a bath of carbonate of soda in order to eliminate the naphthol and to convert the zinc into an insoluble carbonate capable of resisting the subsequent washing. The resist paste, therefore, is a red or a claret combined with carbonate of zinc capable of resisting the black. Prussiate black padded over these azo colours thus rendered basic is perfectly resisted, and it is on this principle that Pluzanski has founded his new style. To associate orange with the red and claret, the diazoparanitrobenzene is replaced by diazoorthonitrolulene. Yellow is got by printing on acetate of lead, which is changed into carbonate in the soda bath, and is finally dyed in a bichromate bath. For black *Noir Reduit* is used, and for white it is merely necessary to print on thickened zinc white, which sufficiently resists the soda bath and a moderate washing before the black is printed on. A style which has a certain resemblance to that of Pluzanski was described by C. Kurz and E. Kunert (*F.Z.* 1897, p. 49). This is a production of para red designs over vat blue. To obtain these, the diazo paste containing acetate of lead is printed over the indigo dyeing prepared with naphthol and chromate of potash. Chromate of lead is formed in mixture with the red. In the acid bath the blue is discharged and the red appears.”

L. Ziegler describes a method which is cheaper and simpler than the pioneer methods of Pluzanski. The process has been made possible by the new Express colours put on the market by Wegelin,

Tetaz and Co., of Mulhouse. These can be fixed on Prud'homme black simply by a short steaming without the use of any agent such as albumen. The resulting colours are quite fast even to strong soaping. This is an important advantage, as mordant dyes can be dispensed with and better fastness is secured than can be obtained with ferrocyanide of zinc mordant, and a basic colouring matter. Ziegler claims also that the colours produced by the Express dyes are the brightest and liveliest hitherto produced in combination with Prud'homme black.

The Express colours are bluish red, yellowish red, pink, yellow, blue and green. The reds are warmer than paranitraniline reds fixed by Pluzanski's method. The goods require no preliminary scouring with carbonate of soda. The following is an illustrative recipe:—

4,000	grammes	British gum,
13,500	..	warm water,
25,000	..	Express Red B or R previously dis-
		solved in water of from 70 to 80° C.
5,000	..	zinc oxide,
2,500	..	ammonia-soda ash.

For pink, yellow, blue and green, the amount of zinc oxide is increased to 7,500 grammes, and the soda ash is dispensed with.

After dyeing the goods are steamed for from two to three minutes in the small Mather and Platt, and then fixed with a $\frac{1}{2}$ per cent. solution of sodium bichromate, rinsed, soaped, rinsed, centrifuged and dried.

CHAPTER VII.—Treatment of the Goods after Printing.

Development of the printed colour varies with the kind of black employed. In addition to one bath black, which is used only in dyeing, we distinguish oxidation black from steam black. Oxidation black includes the printing colours prepared with sulphide of copper, vanadium, chromate of lead, or tungstate of chrome, which are developed by ageing or oxidation at 30 to 40° C.; whereas steam black, such as the prussiate black and even certain chromate of lead blacks, will withstand steaming for twenty minutes without injury to the fibre. However, this distinction between the blacks is of hardly any importance since the invention of Mather and Platt's rapid ager, which enables us to develop all the oxidation blacks by a short steaming without fear of tendering the fibre.

Before the invention of this apparatus the oxidation blacks were developed either by long exposure to the air or in specially constructed oxidising apparatus. Many of these machines are still in use.

Development by ageing is now employed only in a small number of works. The black is developed at a low temperature, and the strength of the fibre is fully maintained, but the operation takes a far longer time than the other methods.

Ageing rooms were used to fix printed mordants on the fibre long before the invention of aniline black. D. Koechlin (*B.S.M.*, 1828, p. 309) was the first to insist on the importance of careful regulation of the degree of humidity in the ageing rooms. The form of hygrometer known as August's psychrometer, is used for this purpose; it consists of two similar thermometers, one of which is constantly kept wet. The dry thermometer should mark 36° C., the one with wet bulb 33° C.

THOM'S AGEING CHAMBER.

John Thom patented in England (*E.P.*, 22,610, 1849) the first apparatus providing for the methodical introduction of moisture into the oxidation chamber. Fig. 5 is an elevation of his apparatus. A flag cistern G is filled with water to the level E, at which height is a pipe and stop-cock to run off the surplus water. The water is heated by steam from a pipe C. The excess of steam from the chamber is passed off by a pipe through the roof D. F are two rows of spars placed under the rollers B, the low ones

being wider than the space between the upper ones, so as to prevent the water below from being spurted on the goods. Above this cistern is a large wooden chamber H, in which are placed two rollers B B. The sides of the chamber are vertical, and the roof is at an angle of about forty-five degrees, so that the condensed steam may trickle along the under-side and be received in a gutter and prevented from falling on the goods. In the sides of the chamber, at the upper part, are two slits for the ingress and egress of goods, and immediately above these slits are rollers K, of greater diameter than the thickness of the side of the chamber, so as to extend inwards and outwards over the side of the box and prevent drops of condense water from falling on the goods. These rollers

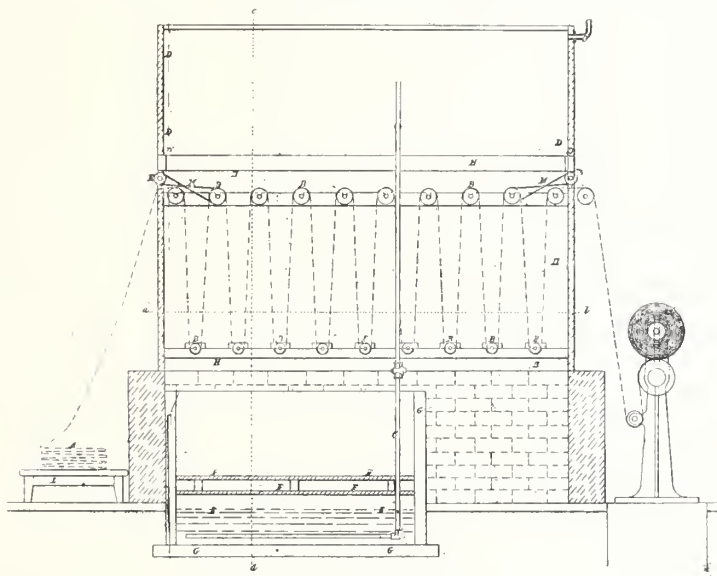


FIG. 5.—THOM'S APPARATUS.

are covered with flannel, and driven from the end of one of the rollers, as shown at M. The goods being placed on the stool L, and the water heated to about 180° F, vapour rises from the surface of the water in the cistern and passing between spars, fills the chamber. The goods to be aged are passed through the chamber, and on leaving are wound on a roller or plaited down. The goods so operated on will be found to contain nearly an ounce of moisture for every pound of dry fabric. The goods, after being so treated, may be raised or dyed immediately, or hung up in the usual manner on rails or tenter hooks previous to being raised or dyed. It will be obvious, that alterations may be made in the details for the purpose of subjecting the fabrics to the action of gas or water vapour.

Walter Crum erected a large apparatus on Thom's principle, and this is described in Crooke's well-known work on dyeing:—

“ This process was at one time performed in enormous chambers

known as ageing rooms. In these chambers the goods sometimes remained for five or six days, hung up in single folds, so as to be in full contact with the hot moist air. It was then found that this exposure in single folds was not necessary, and that the absorption of oxygen, etc., might be sufficiently carried on if the pieces are laid in heaps upon sparred floors in the ageing room, thus effecting a great saving in space. A most marked improvement, which reduces the time needed for the process from several days to as many hours is the ageing machine introduced by Mr. Thom and Mr. Crum, and now in general use. This machine as manufactured by Messrs. Mather and Platt, of Salford, is a chamber 36 feet in length, 20 high and about 13 broad, through which the pieces, by means of a system of rollers, at such a rate as to be 20 minutes in passing. The requisite temperature and degree of moisture are kept up by means of steam pipes fitted with bell-shaped openings for diffusing the vapour. After this passage through the machine the pieces are collected in loose bundles and left over night on the floor of an outside chamber, which is kept at the same degree of heat and moisture as the interior of the machine. The temperature of the ageing rooms or ageing machines is generally fixed at 70 to 75 or 80° F., the moisture being regulated about 4 degrees lower. For this purpose pairs of dry and wet bulb thermometers are fixed in different parts of the chambers. According to well-known physical laws the nearer the atmosphere of any place is to saturation with moisture the more nearly does the temperature indicated by the wet bulb thermometer approach that shown by the dry. If the wet bulb instrument falls below the point fixed upon as giving the best results, more steam is admitted, but if it approaches too near the temperature, the supply of steam is decreased. In every arrangement of ageing appliances sudden changes of temperature have to be duly guarded against, as a condensation of steam might occasion much trouble. Hence the doors, windows and roof of the exterior chamber into which the pieces are removed from the machine are generally made double. It may be remarked that the chemical and physical changes which take place in ageing are even yet not so fully understood as might be desired, and that there is consequently room here both for chemical and microscopical research. Thierry Mieg, of Toulouse, proposes to improve the ageing rooms by introducing along with the steam a current of hot air. These heated chambers are to serve both for fixing the mordants printed upon the goods in the madder styles, and as a steaming apparatus for steam styles. For the former purpose the idea seems sound. The first purpose of ageing is to fasten the mordants by heat and moisture, removing a portion of the acetic acid, so that the iron and alumina may remain in the form of insoluble basic salts. Real oxidation is necessary only in cases of catechu or mordants consisting of proto-acetate or proto-muriate of iron (ferrous acetate and chloride). In both cases the ventilation of the ageing rooms is often insufficient. The chamber becomes so filled with a vapour of

acetic acid that its further escape from the mordants upon the cloth is rendered impossible. The oxygen is used up quickly, even in the old rooms, where the pieces hang for three or four days, and this is still more the case in the ageing machine. It is thus rendered difficult to obtain a full catechu brown, however strong the colour, because the development of catechu shades requires a certain amount of oxygen, while the addition of nitrate of copper to the printing mordant, as an oxidising agent, cannot be carried beyond certain limits. The introduction of a current of warm air remedies both the imperfect ventilation and the deficiency of oxygen. M. Thierry Mieg proposes, however, to carry the temperature of the ageing room up to 212° F, which for fixing mordants is not only needless, but in case of aluminium mordants hurtful, as far as present experience goes."

Aniline black can be developed perfectly well in ageing rooms intended for the fixation of mordants. When the black is printed together with mordants, the pieces should be hung up a sufficient time to fix the mordants. When it is printed alone six to seven hours in the ageing room is sufficient time to oxidise it.

By increasing the acidity of the printing colour, the development of the black can be accelerated in some degree. The temperature should be 40 to 45° C., the wet bulb thermometer marking at least 6° less.

Zuercher (*B.S.M.*, 1885, p. 319) notes that aniline black develops badly, or not at all, when the printed pieces are submitted to a current of cold air before the colour is oxidised. The aniline appears to be volatilised. The black does not develop well unless the temperature is at least 25° C.

Kertesz makes the following note on this subject:—"At a Dusseldorf works I had a batch of goods in a slightly warmed room, and it happened that several panes of glass were broken in the windows on one side. The following morning the pieces had developed normally, with the exception that the parts of the cloth exposed to the direct action of the current of air were grey, and subsequent treatment in an oxidation chamber at a relatively high temperature failed to improve matters."

PREIBISCH'S OXIDATION APPARATUS.

C. R. Preibisch (*E.P.*, 12,472, 1884) protected a system of oxidising aniline regularly and continuously. This apparatus has been used in Germany and elsewhere, and has also been made in France. It is constructed to-day just as described in the specification, with the exception that the fans G have been taken out in order to make room for more reels.

The apparatus, shown in longitudinal section in Fig. 6, and in end section in Fig 7, consists of an iron frame covered by wooden walls, with alternate doors and windows in the sides, so that the process may be watched and access to the fabric gained at all parts. At the bottom there is a system of heating pipes H; just above

these is a series of loose reels *F*, and just under the roof of the chamber are another set of reels *E* set off from the lower ones by a distance equal to the diameter of the reels. The second set of reels carry at one end outside the chamber a number of bevel wheels of equal size which are set in uniform motion by bevel wheels, also of even size, on shaft *D*.

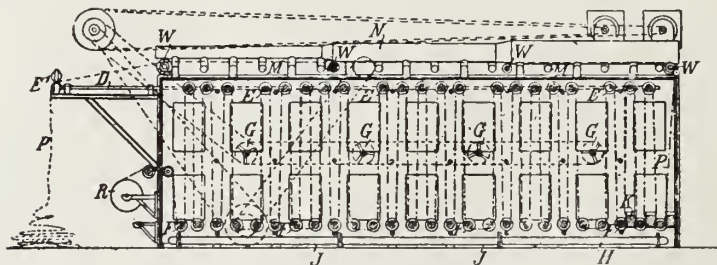


FIG. 6.—PREIBISCH'S APPARATUS.

The fabric *P* saturated with the dyebath is wound up on a reel *R* carried in bearings on the forward end of the chamber. Through a slot in the front of the apparatus the fabric is introduced and alternately led over the loose reels at the bottom and the upper reels.

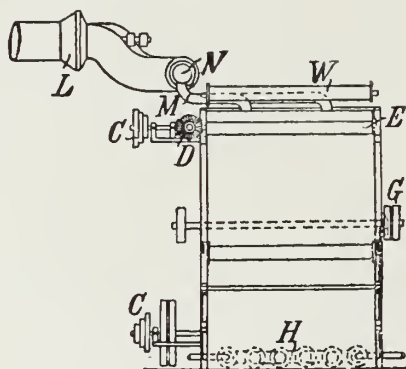


FIG. 7.—PREIBISCH'S APPARATUS.

By the uniform rotation of the whole of the upper reels *E*, the fabric rises and descends over the reels in a state of even tension, and at a uniform rate and is drawn out of the apparatus by the drawing-out roller *E*¹ which is also driven by the shaft *D*.

A temperature of 44 to 50° C. is maintained within the apparatus by means of the heating pipes. For the purpose of causing the drying of the goods to take place as rapidly as possible with this comparatively low temperature the interior of the apparatus is connected with two exhausts *L* which continually draw the air off. The inflow of air takes place through apertures in the front part of the apparatus. To distribute this air as evenly as possible within the apparatus and for the purpose of directly fanning the fabric, four fans *G* were at first provided in the apparatus.

As the temperature in the room from which the inflow of air is

taken is always maintained at 25° C. the process of drying the fabric progresses very rapidly in the apparatus.

To remove as quickly as possible the gases liberated during the drying by the oxidation of the mordant which would attack the fabric if left in contact with it for any length of time numerous branch pipes M lead from the main suction pipe N of the two exhausters L and these are evenly distributed upon the roof of the apparatus throughout its length..

In consequence of this arrangement the injurious gases which are evolved are directly removed from the interior of the apparatus by the shortest way, so that they cannot exert any injurious influence upon any other part of the fabric.

As soon as the fabric has passed through about two thirds of the apparatus it is perfectly dry and the oxidation has been effected, so that the fabric begins to become coloured. As it is well known to be important for the successful production of a good black that the development of the colour should take place in a moist atmosphere this end of the apparatus is completely closed at the lower end, so that no drying current of air can enter here, and several receptacles K with water are provided, the evaporation of the water producing a sufficient degree of dampness.

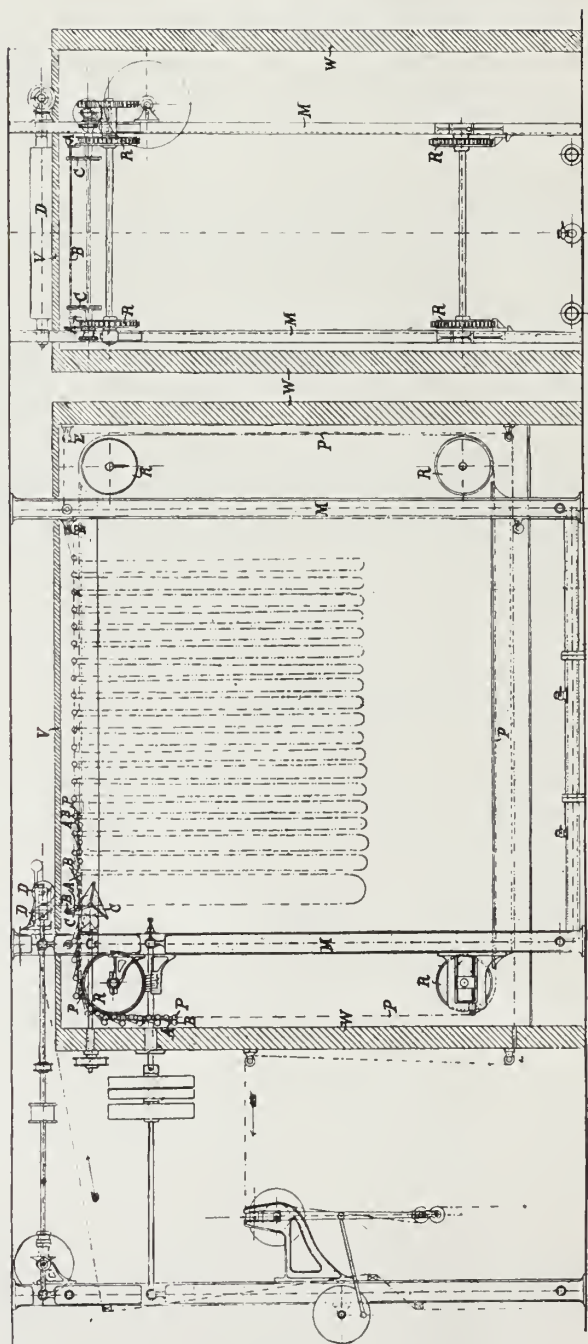
The fabric then issues from the apparatus at its upper part and is led by guide rollers W over the entire apparatus and to the front; during this movement it becomes once more perfectly dry and cooled, and may be folded or cuttled.

To enable the apparatus to be used with equally good results both for light and heavy fabrics a stepped pulley C is employed so that the speed at which the fabric moves may be reduced or increased as desired. If the apparatus is built for very wide fabrics, two narrow fabrics may be passed through it simultaneously side by side.

The apparatus can be used not only for cotton goods but for half woollen also. With the processes hitherto used in dyeing aniline black, this was not practicable as the woollen parts assumed a dead dirty colour, and absolutely lost the capacity for being dyed to a better black. Preibisch claims that with this apparatus the weft does not suffer any loss of brilliancy, and can be dyed to any desired black tint by logwood; goods thus produced are characterised not only by the fastness of their colour and their fine appearance, but their feel is also very soft and pliant. Experiments with half silk goods have likewise given favourable results.

REMY'S OXIDATION APPARATUS.

Another apparatus, patented in all countries (*E.P.*, 20,905, 1889), was invented by Emile Remy, partner in the firm of J. Heilmann and Co., Mulhouse. The principal improvement is that the cloth is automatically shaped into long folds that hang side by side so that the material offers a large surface to the gas, steam or hot air.

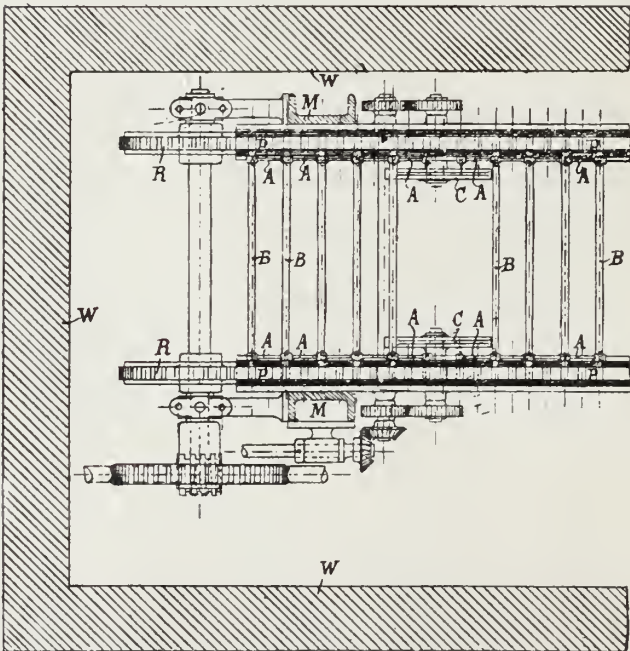
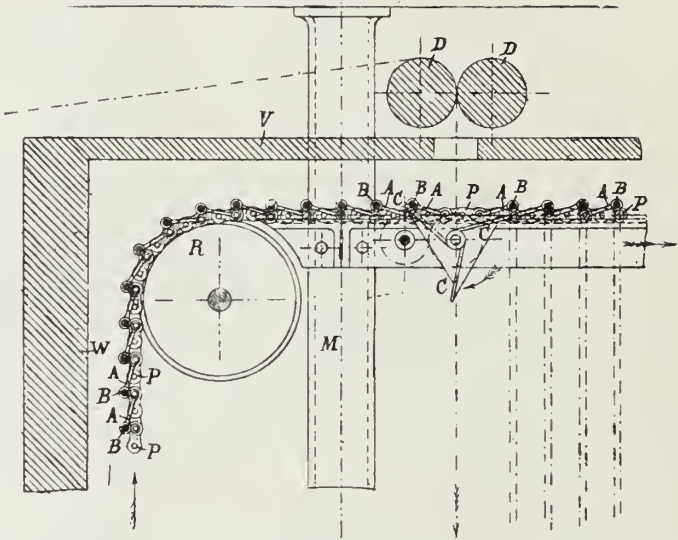


FIGS. 8 AND 9.—REMY'S APPARATUS. LONGITUDINAL AND END SECTIONS.

Fig. 8 is a longitudinal section, and Fig. 9 a cross section of the apparatus.

Within a chamber having side and ends walls W and a cover V, are vertical uprights M that carry the moving and guiding mechanism. This comprises eight chain wheels R, divided into two sets, each consisting of four wheels lying in a common vertical plane, and surrounded by an endless chain P. The two chains each receive a travelling motion from one or more of their chain wheels R. To the links of the chains are attached short arms A, each capable of turning about a centre. Each two of these arms constitute a set, and in corresponding positions on the two chains are connected together by a roller B. When the chains are travelling, each set of two arms thus connected will, at the entrance end of the apparatus, hang in a downward position, and in a contrary direction to that in which the chains are travelling. Near to the point at which the material to be treated is fed into the apparatus by rotating feed rollers D D, is mounted a set of turnstiles C, capable of rotating at a higher speed than the travelling speed of the endless chains.

If now the material to be treated enters the apparatus between the endless chain in a downward vertical direction, as indicated by dotted lines, the revolving turnstiles will take underneath the next rod arriving with the travelling chains, and will lift the rod with its two arms and will turn the rod and arms over in the opposite direction, that is, in a forward direction, so that the arms are then in a position corresponding with the travelling direction of the chains. By the lifting of the rod it is brought against and underneath the entering material, which in continuing its downward travel will form a vertically hanging fold, until the turnstiles lift the next rod and bring it underneath the entering material so as to form a second fold similar to the first. As the endless chains continuously travel onward and the turnstiles after the turning over of a rod are somewhat retarded in their rotation, there will always be an appropriate period between the action of the turnstiles on two successive rods, for the automatic formation of the material into folds one after the other. The length of the folds can be regulated at will. This action of turning the rods over from a rearward into a forward position is constantly repeated, so that the material travels with the chains through the greater part of the length of the chamber in long hanging folds until it arrives near the end of the uppermost portion of the length of the chains. Here the material is conducted over guide rollers E and either directly leaves the apparatus, or is guided downward and then horizontally below the endless chains P as shown, back to the entrance side of the apparatus. This latter course is most advantageous because the material will remain longer in the chamber and will consequently be further subjected to the influence of the gas, steam, or hot air.



FIGS. 10 AND 11.—REMY'S APPARATUS. DETAIL AND PLAN.

In Figs. 10 and 11 that part of the apparatus at which the material enters and the rods B are turned over from their backward to their forward positions by the turnstiles C, is shown to a larger scale than in Figs. 8 and 9. The chamber may be provided with apertures for the exit of moisture, and may be placed in communication by these apertures with ventilators or exhausters for the removal of moist air.

The apparatus has the great advantage of not condensing the steam or vapour, as the endless chain with its rods always remains inside the chamber, and consequently always maintains the same temperature at the interior. The correspondence between the heat and the humidity can be easily regulated, and the machine does not require much attention.

MATHER AND PLATT'S RAPID OXIDATION APPARATUS.

The "Ager," now known in universal technical literature as the "Mather and Platt," was invented in 1879. It allows the various printing blacks and the ferrocyanide of aniline padded black to be developed by a short steaming of one to three minutes.

H. Schmid (*W.J.*, 1882, p. 902) reports that this apparatus was in use for the continuous oxidisation of aniline black from the year 1880 onwards.

Schmidlin's black, which is slightly acid, is developed particularly well in this apparatus. Many other blacks are equally well developed, such as chlorate of ammonia and aniline salt, chlorate of aniline and a salt of copper, or aniline salt, an alkaline chlorate and ferro or ferri-cyanide. Aniline black is now almost universally developed in the Mather and Platt to the exclusion of ageing rooms.

The introduction of basic salts of aniline largely contributed to the extended employment of this important apparatus which has proved so valuable to the textile colouring industry.

The chamber is supplied with steam through a perforated pipe running along the base of the apparatus. The working temperature of the chamber for this class of work is about 77° C. and 74 hygro-metric degrees, and the pieces pass through at the rate of about 60 metres per minute over copper rollers driven by a small steam engine or electric motor.

The greatly increased output of Mather and Platt's rapid oxidisation process has enabled it to supersede the old method of oxidisation by prolonged hanging. It allows the Prud'homme style, invented shortly after the introduction of the Mather and Platt, to be easily produced, whereas the oxidisation processes cause the discharge colours to lose their vivacity by reason of the prolonged stay in the oxidising chamber. Prussiate black does not develop well at a temperature of less than 95° C., and a steaming of more than three minutes at this temperature would tender the fibre.

The pieces are not tendered by a passage through the apparatus. The printed or padded prussiate black is oxidised at 95° C. The sulphide of copper black is developed between 65° and 70° C., and

for this and other printed blacks of the same kind, such as the chromate of lead and the vanadium blacks, the Preibisch apparatus, which oxidises more slowly, and at a lower temperature, is preferable. The Mather and Platt, however, is more economical, and in work where the Prud'homme style is turned out, all the blacks are dealt with in the ager.

In the case of the printing black the degree of humidity in the oxidising apparatus is of no great importance; it is sufficient to keep the temperature up to the required degree. On the other hand, the success of the Prud'homme discharged style depends largely on the amount of moisture and the composition of the atmosphere in the oxidising apparatus. The apparatus should be ventilated either by means of a ventilating shaft or a shaft in combination with a fan. The fan provides the best means of ventilation, but, unfortunately, its iron wings are speedily destroyed by the action of the acid vapours given off during oxidation.

C. Brandt (*R.M.C.*, 1900, p. 193), notes that the tendering of the fibre and the yellow tinging of the discharged whites during the development of the aniline black can be avoided by constantly renewing the atmosphere of the chamber. To effect this the room in which the apparatus is worked must be heated so that a constant supply of hot air can be sucked into the machine. As the pieces leave the apparatus they pass under this current of in-flowing air, and are thus freed from the gases developed in the oxidation of the aniline, which adheres to the surface of the cloth to some extent. This system is excellent, but expensive.

In the running of the Mather and Platt the exhaust steam from the engine which drives it is sufficient to supply the steam chests. Condensed steam (i.e., water drops) is prevented from dropping on the cloth by fixing a steam-heated pipe over the entrance to the apparatus. A syphon at the bottom of the chamber draws off the condense water.

Practical experiment has proved that printed or padded prussiate black, when it is properly prepared, will withstand the action of steam superheated to 114° C., but neither the black nor the discharges are better than when the temperature does not rise above 95° C.

The rapid development of the aniline black by the energetic action of the Mather and Platt increases the chance of tendering the cotton fibre if care is not taken to prepare the printing colour correctly.

THE LATEST MATHER AND PLATT MACHINES.

Messrs. Mather and Platt have recently introduced improvements in their oxidising apparatus for aniline black. Fig. 12 shows the new oxidising machine with a hot air drying chamber, brought out in order to cope with modern requirements.

As a matter of fact, oxidising processes in print works have undergone such an extension that in order to deal with the goods

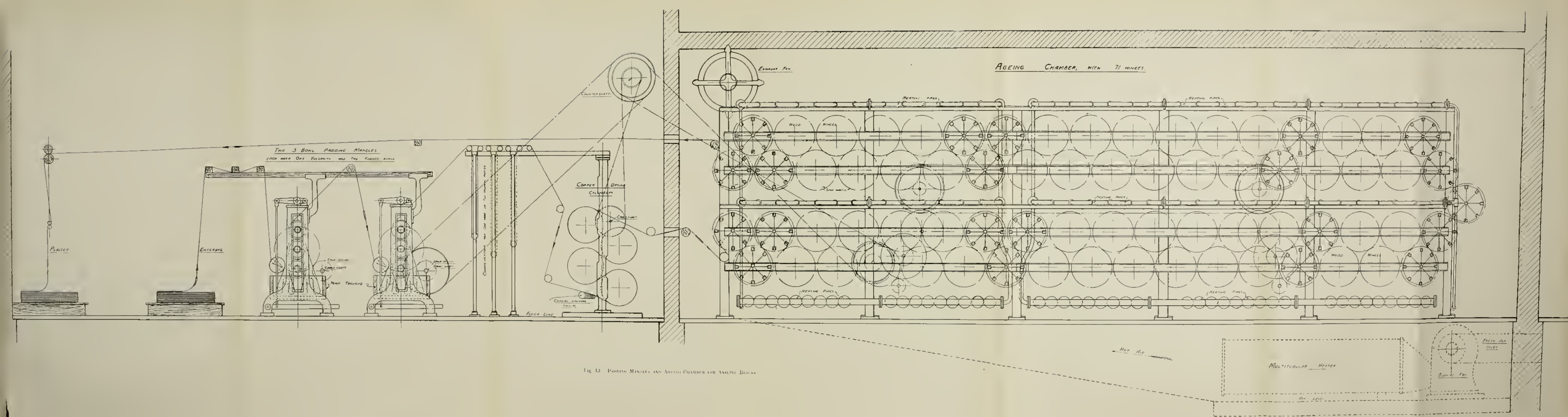


Fig. 13. Padding Mangle and Ageing Chamber for Aniline Blacks

in a satisfactory manner it has become necessary to replace the older machines by much more important installations.

It has become necessary to have an apparatus capable of drying both sides of the piece in an absolutely even manner and without the slightest variation of the colour. The machine should be capable of easy adaption to the special conditions of the oxidising process; the hot air should be introduced in such a way as not to cause too prompt an oxidation of the colour on the selvages; the goods should run through the machine at a high speed without scrimping; the vapours should be evacuated completely; the whole interior of the machine should be easily accessible; and the run of the goods should be visible from one end to the other.

All these highly important conditions have been realised in the apparatus shown in Fig. 12. Although the machine has been introduced quite recently, it has already been adopted in many print works in Great Britain and abroad. The drying chamber can be placed on the same floor as the oxidising machine or on another storey of the building.

The installation for drying, oxidising, and steaming aniline black is shown in Fig. 13. This machine is frequently employed for goods printed with sulphide of copper oxidation black. It ensures a large output and completely avoids scrimps and tears. The machine is generally constructed to take either one broad piece or two narrow pieces running side by side.

The apparatus includes two padding machines with indiarubber or vulcanite rollers, with the usual compound levers and weights for giving the necessary pressure on the nips.

The material passes over the stretching rollers in front of the first padding machine into the padding bath; from there it passes between the lower and middle squeezing rollers and returns to the bath; it then passes between the middle and upper squeezing rollers and thence to the second padding machine, where it again passes twice through the bath and is given two nips.

After leaving the second padding machine the material passes over compensating rollers which regulate the tension on the cloth between the padding and drying machines; it then passes over the drying cylinders and direct into the ageing chamber, going first over the two lower rows of winces, then back over the two higher rows, to be finally delivered from the same end of the ager as that through which it entered.

The steaming chamber has from 50 to 100 winces geared together with wheels as in an ordinary cylinder drying machine, and the material is in contact with them from its entrance to its exit. The chamber is kept at a given temperature by means of two rows of wrought iron pipes and a row of cast iron pipes running the whole length of the chamber and heated by steam. The heating is effected in some measure by hot air blown in by a fan at the bottom of the chamber through a multitubular heater; the evacua-

tion of the hot air is effected by means of a fan mounted in the roof of the chamber.

The necessary degree of humidity in the steaming chamber is attained by means of direct steam blown in through very fine perforations in a steam pipe, resting on the floor of the chamber; and it may be regulated by valves provided for this purpose.

The installation is driven by a steam engine or an electric motor.

The construction described allows the work to proceed continuously and uninterruptedly from the first roller to the final plaiting down.

OTHER MACHINES.

Some of the leading firms of engineers on the Continent also make special forms of steaming and oxidising apparatus. Fig. 14 is the oxidising machine of the Zittauer Maschinenfabrik of Zittau i/S, Germany, and Fig. 15, the steam ager of the same firm.

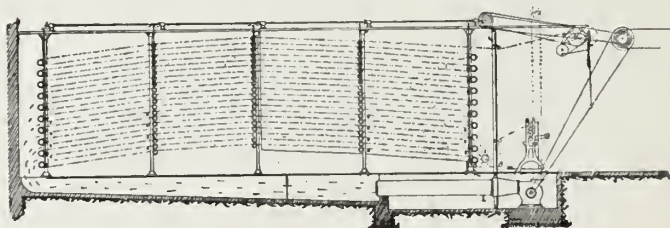


FIG. 14.—OXIDISING MACHINE WITH PADDING MANGLE.

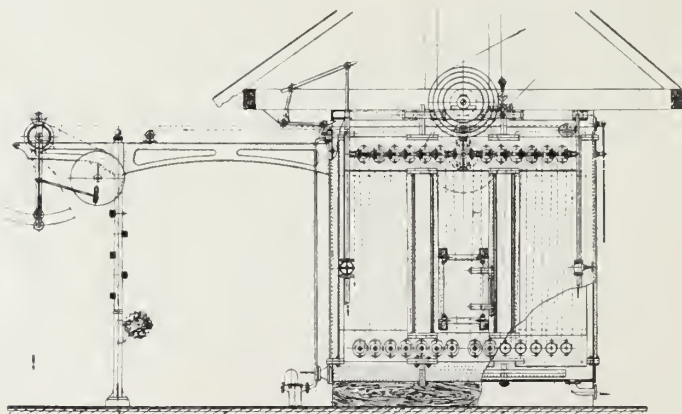


FIG. 15.—STEAM AGER.

CHAPTER VIII.—Causes of Tendering of the Fibre and the Methods of Prevention.

F. Beltzer (*R.G.M.C.*, 1902, p. 113) made a series of experiments with the view to determine the part played by each of the constituents of the aniline black bath in the tendering of the fibre. A hank* of 100 metres of yarn stood a strain of 37.05 kilos. before treatment. The following bath was used:—

A.—1,250	grammes	aniline oil,
1,100	„	hydrochloric acid, 22° B.
125	„	tartaric acid,
5	litres	water.

Bring up to $7\frac{1}{2}$ litres with water.

B.—200	grammes	chlorate of potash,
175	„	sulphate of copper.
250	„	sal ammoniac,
$7\frac{1}{2}$	litres	water.

Mix A. and B., dye and develop the emeraldine at 50° C. for ten hours, chrome with 30 grammes bichromate per litre, wash, soap and dry. The breaking strain is now only 29.5 kilos., a loss of 20.9 per cent. as compared with the undyed yarn.

Similar hanks were then treated in the following solutions, of the same concentration as in the dye bath, and dried at 70° C.

	Breaking strain.
Undyed yarn	37.05
Chlorate of potash	37.05
Sulphate of copper	20.00
Chlorate and sulphate	5.00
Chlorate, sulphate and free hydrochloric acid	0.00
Solution B.	9.00
Solution A.	33.00
Solution A. and sulphate	29.00
Solution A. and chlorate	20.00
Solution A., chlorate, sulphate and hydrochloric acid	0.00

*The word "hank" is used loosely here, simply to convey the meaning of reeled yarn. A hundred metres is less than a lea, a little over 109 yards. Tr.

The tendering of the fibre therefore is caused by the free hydrochloric acid and chlorine from the chloric acid. An experiment with acetate of copper and chlorate of potash showed no tendering of the fibre, but the black was not developed; the acetic acid being volatile is driven off on steaming, and the emeraldine is not produced on the neutral ground.

This unfortunate weakening of the fibre in aniline black dyeing is due to the chemical transformation of the cellulose into hydrocellulose and oxycellulose.

Hydrocellulose was obtained and described by Girard (*C.R.*, lxxxi., p. 105). He prepared it by wetting out cellulose and submitting it for twelve hours to the action of sulphuric acid at 15° B., or by impregnating the cellulose with a weak solution of acid and drying at 100° C. The cellulose then loses all its resistance; in the moist condition it preserves its initial structure, but is reduced by drying to a friable substance giving a white powder, to which Girard assigned the formula $(C_{12}H_{22}O_{11})_n$.

Cellulose, $C_6H_{10}O_5$, is thus transformed into a hydrated modification from which the water cannot be extracted by dessication.

Girard (*M.S.*, 1879, p. 958) proved in a later research that cotton is transformed into hydrocellulose by the action of moist hydrochloric acid gas. It is not only produced by this means, but by the action of all the mineral acids with the exception of sulphuretted hydrogen and sulphurous acid. Completely dry hydrochloric acid gas has no action on equally dry cellulose. Girard considers that this proves that hydrocellulose is the result of hydration.

Cross and Bevan ("Cellulose") state that hydrochloric acid and sulphuric acid of a specific gravity of 1.3 give the same hydrocellulose, whereas sulphuric acid of Sp.G. 1.5 to 1.6 gives a hydrated modification of cellulose with the formula $(C_{12}H_{22}O_{11})_n$, but widely differentiated from hydrocellulose and with the property of being termed blue by iodine, whence it has been termed "amyloid." It reduces oxide of copper in alkaline solutions and forms a gelatinous modification, which, when cellulose is worked up into paper, is called vegetable parchment.

In the formation of aniline black the hydrocellulose described by Girard alone comes into play. To prevent its formation during the development of the black, the printing or padding colour must be composed in such a manner that the hydrochloric acid of the aniline salt is rapidly and completely deprived of its power of tendering the fibre. The addition of ferrocyanide of potassium effects this desired result by forming chloride of potassium in combination with the hydrochloric acid of the aniline salt.

Grawitz (*C.R.*, 113, p. 745) attributes the formation of hydrocellulose during the development of aniline black to the production of a monoacid tetramine with the formula, $C_{24}H_{20}N_4$, formed by four molecules of hydrochloride of aniline, and consequently freeing three molecules of hydrochloric acid. By using three-quarters of the aniline in the state of acetate the danger of an

excess of free hydrochloric acid is avoided but a fine black is not obtained.

METHODS OF AVOIDING TENDERING.

Many experiments have been proposed to prevent the formation of hydrocellulose, especially since the invention of the Mather and Platt, but no really advantageous substitute for the mineral acids has been discovered.

Thiess and Cleff (*D.R.P.*, 57,467) patented the use of hydrofluoric acid. Hydrofluoride of aniline in paste form has been sent out for some time past by the Farbenfabriken vorm. Fr. Bayer and Co. Its employment prevents the tendering of the fibre. The process for dyeing cotton and silk and cotton is as follows:—

50 grammes	nitrate of copper,
6,000 „	hydrofluoride of aniline,
10 litres	cold water.

This solution is made in a wooden beek, and a paste is made apart with:—

600 grammes	starch,
1,200 c.c.	chlorate of potash,
25 litres	water.

Boil and stir until it cools, then mix the two and bring up to 50 litres.

Work the goods in this bath, dry at 40 to 50° C., and oxidise for a quarter to half an hour at 50° C. dry bulb and 42° wet bulb, chrome and soap.

The fluoride does not seem to have been used on a large scale: it attacks the dyer's hands.

Boehringer and Sons (*D.R.P.*, 96,600) proposed to replace the hydrochloride of aniline by the lactate. Lactic acid does not tender the fibre, and its salts are much more soluble than the tartrates.

Goldowsky (*B.S.M.*, 1900, p. 101) gives the following recipe for a lactate of aniline black which he has used with success.

2,000 grammes	aniline oil,
1,500 „	hydrochloric acid, 21° B.,
250 „	lactic acid, 27° B.,
600 „	chlorate of soda,
500 „	sulphate of copper,
550 „	sal ammoniac.

Bring up to 10 litres with water.

Scheurer and Schoelkopf (*B.S.M.*, 1901, p. 102) compared the above padding bath with another in which the lactic acid was replaced by tartaric acid. After a passage through the Preibisch the shades were identical. The resistance of the undyed cloth

being taken as 100, that prepared with lactic acid was 63 and that with tartaric acid 60. From this it appears that lactic acid attacks the fibre to a somewhat less degree than tartaric acid.

Eberle's patent of 1895 states that the addition of formiate of aluminium to the printing colour is useful. The aluminium neutralises the hydrochloric acid and the formic acid preserves the fibre from the too energetic attack of the chlorine compounds. Acetate of aluminium had already been proposed, with the same object, and is still used in piece and yarn dyeing.

Beltzer's attempts to replace hydrochloride of aniline by the borate, tartrate, arseniate and phosphate will be mentioned later. These attempts do not seem to have led to practical results so far. Arsenic is forbidden in most countries for obvious reasons. and phosphoric acid is too expensive.

Beltzer also tried boro-tartrate and arseniotartrate.

Arseniotartrate black.

- | | |
|---------------|--------------------|
| A.—100 c.c. | aniline oil, |
| 65 .. | arsenic acid, |
| 20 grammes | tartaric acid, |
| 60 c.c. | glycerine. |
| | |
| B.—20 grammes | acetate of copper, |
| 20 .. | sal ammoniac, |
| 20 .. | chlorate of soda. |
| 5 .. | tartaric acid. |

Mix A. and B., bring up to 1,200 c.c. by adding water, impregnate the cotton, and dry at 70° C. for six hours in moist air. The well-developed emeraldine is converted into black by chroming.

Phosphotartrate black.

- | | |
|---------------|-------------------------------|
| A.—100 c.c. | aniline oil, |
| 55 .. | orthophosphoric acid, 45° B., |
| 15 grammes | tartaric acid, |
| 60 c.c. | glycerine |
| | |
| B.—20 grammes | acetate of copper, |
| 20 .. | sal ammoniac, |
| 20 .. | chlorate of potash. |
| 5 .. | tartaric acid. |

Mix A. and B., make up to 1,200 c.c., and proceed exactly as above. These processes may be of interest to dyers.

As we have already said, the second cause of the tendering of the fibre in steaming is the action of the chlorate which oxidises the cellulose and transforms it into oxycellulose.

Witz (*B.S.R.*, 1882, p. 416, and 1883, p. 169) made a research on the formation of oxycellulose by the action of chloride of lime on the fibre. He found that the cotton is modified and acquires the property of fixing the basic colours without mordant and of

separating the metallic oxides from their salts and fixing them, as, for instance, sulphate of alumina, in this way resembling the animal fibres. The resemblance goes still further; aniline black develops as badly on oxidised cotton as on wool.

Witz obtained oxycellulose by treating the cotton for an hour in chloride of lime at 2° B. Ozone and hydrogen peroxide act in the same way. Witz hoped to realise some new and interesting effects on cotton cloth by taking advantage of this action, but the idea had to be given up as the oxidation is always accompanied by a proportionate tendering of the fibre.

Cross and Bevan have published several volumes of important "Researches on Cellulose." Nitric acid, Sp. G. 1.1 to 1.3, converts cellulose into oxycellulose; it gives a white flocculent mass, which, on the addition of water, is converted into a gelatinous hydrate. Cross and Bevan have only been able to convert 30 per cent. of the treated cotton into cellulose in this manner. They conclude that the molecule of cellulose is composed of a stable nucleus, and of easily oxidised lateral groups.

V. Faber and Tollens (*Ber.* 32, p. 2,589) have nevertheless been able to raise the percentage to 70 by oxidising with nitric acid of Sp. G. 1.3, and A. Nastjukoff has obtained more than 90% by heating cellulose impregnated with nitric acid of the same strength in the water-bath for an hour. He shows that a more energetic oxidation transforms the oxycellulose into oxalic acid, and this explains the poor yield obtained in the first experiments. This oxycellulose is soluble in dilute alkalis.

When cellulose is oxidised with hypochlorous acid, a second modification of oxycellulose is produced, especially in presence of carbonic acid. This has the property, according to Cross and Bevan (*J.S.C.I.*, 1884, p. 206, 291) of fixing the basic colours directly. This modification corresponds with the first described by Witz. It has been studied by H. Schmid (*D.P.J.*, 250, p. 271), Noeltig (*B.S.R.*, 1883, p. 160, 239), and others.

Nastjukoff (*B.S.M.*, 1882, p. 493) states that the most highly oxidised product of cellulose is an oxycellulose, with the empirical formula $C_6 H_{10} O_6$, and this easily dissolves in cold dilute alkalis. It is recognised by its ability to fix basic colours without a mordant. Methylene blue is a good test.

The cause of the formation of oxycellulose is the chlorate in the printing colour. The danger of tendering the fibre by this means is always much less than by conversion into hydrocellulose by the acids set at liberty. Care must therefore be taken to neutralise the mineral acids promptly, and to calculate by preliminary trials the exact proportion of chlorate necessary for the development of the black.

AFTER-CHROMING OXIDATION BLACK.

Aniline black developed by oxidation, and in particular that

oxidised in the Mather and Platt, usually requires a super-oxidation with bichromate, in order to obtain an ungreenable black. This treatment is absolutely necessary in the case of prussiate black, whether dyed or printed. The chroming is done either in a cold or a hot bath, containing 5 to 30 grammes per litre of bichromate of soda, to which some chalk is often added to neutralise the free chloric acid. The chroming is done in the jigger, which is too well known to require description.

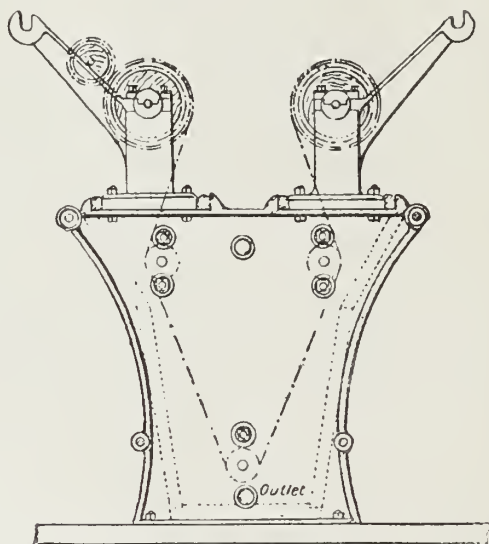


FIG. 16.—LANCASHIRE JIGGER.

The tone of the prussiate black is greatly modified by the passage through chrome; to obtain perfect evenness the temperature and the concentration of the bath must be kept constant. The bath should be tested therefore from time to time with Mohr's salt, or better still, with tin salt.

CHAPTER IX.--Aniline Black on Wool and Silk.

It was very early recognised that aniline black would not develop as well on wool as on vegetable fibre. Lightfoot (*E.P.*, 2,327, 1865) attributed the cause to the reducing action of the wool, and in order to obviate this he chlorinated the wool before dyeing or printing. The material is passed through the following bath:—

1,300 grammes	chloride of lime solution,
180 „	hydrochloric acid,
60 litres	water.

The wool is treated in this bath at 38° C. until it takes a yellow colour. The chloride of lime solution is prepared by dissolving 1 kilo. of dry chloride of lime in 10 litres of water. Wool thus prepared is printed with Lightfoot's or Lauth's black and the colour is developed by ageing.

Jules Persoz (*B.F.*, 77,607, 1867) mordants the wool to begin with for an hour at the boil with 5 grammes of bichromate of potash, 3 grammes of sulphate of copper, and 2 grammes of sulphuric acid per litre of water, washes and dyes in a second bath of oxalate of aniline at 1 to 2° B.

Persoz expressly states that the relative proportions of the mordant and the colour may be modified, and that the specified salts may be replaced by others. In his English patent (*E.P.*, 2,843, 1867) he says that the aniline salt should be used in a hot bath, and that the dyeing may precede the mordanting. He also says that the wool can be dyed by the one-bath process in a cold bath containing the aniline salt and the bichrome.

Reimann, writing in 1868, directs that either wool or silk should be treated in a hot bath of 500 grammes of sulphate of copper, 250 grammes of chlorate of potash, and 250 grammes of bichromate of potash, in 5 litres of water, the dye bath being made with a solution of any aniline salt. The mordanting and dyeing are to be repeated until the black is sufficiently intense.

None of the processes so far mentioned are practical.

Gonin and Glanzmann (*B.F.*, 82,552, 1868) recommend for printing or dyeing wool or silk in aniline black the use of a mixture of 100 grammes of chlorate of potash, 100 grammes of sal ammoniac, and 250 grammes of hydrochloride of aniline, or other salts of aniline, its homologues, or derivatives, together with 125 grammes of nitrate of copper or other salt capable of causing or quickening the oxidation. The colour is to be developed in a hot and moist ageing room. For a printing colour it is to be thickened in the usual way, and after printing developed as above.

Le Moniteur de la Teinture, in 1870, gave the following process for dyeing aniline black: 1 kilogramme of wool is impregnated with a solution of

90 grammes	permanganate of potash,
135 ,,	sulphate of magnesia,
5 litres	water.

The wool is then dyed in a second bath containing hydrochloride of aniline and after-chromed.

Homme (B.S.R., 1876, p. 263) suggests the use of the salts of vanadium for the production of a fine black on wool. The bath contains:

80 grammes	aniline salt,
40 ,,	chlorate of potash,
$\frac{1}{10}$,,	vanadate of ammonia.
5 to 10 ,,	hydrochloric acid,
1,000 ,,	water.

Homme insists that this excess of free hydrochloric acid is indispensable to obtain a fine black. He believes that the wool always retains some free alkali from the suint, and that it is necessary to neutralise this with hydrochloric acid. The black is developed after dyeing in a heated ageing room. Homme states that it is useless to prepare the woollen with bichrome and sulphate of copper. He makes no mention of the preliminary chlorination of the wool, which he does not seem to have studied.

Delory (W.J., 1879, p. 1,086) gives a process of dyeing aniline black on wool or silk. He treats 250 grammes of wool in a boiling bath containing 100 grammes of bichromate of potash, 100 grammes of sulphuric acid, and 10 litres of water, leaving the goods in the bath until it cools, and then dyeing with 30 grammes of aniline salts and 55 grammes of bichrome in 10 litres of water. The goods are entered into the cold bath, which is then heated to boiling point or a little under.

As wool is tendered by dyeing with 5 per cent. of its weight of bichromate and 3 per cent. of sulphuric acid, it is not to be supposed that it will withstand a treatment with 40 per cent. of each of these products as in this process.

For silk, Delory mordanted with

5,000 grammes	bichromate of potash,
6,000 ,,	sulphuric acid,
100 litres	water.

and dyed in a bath prepared by mixing the two following solutions:

100 grammes hydrochloride of aniline,
30 litres water.

175 grammes bichromate of potash,
150 „ sulphuric acid,
3 litres water.

This dye bath is for 1 kilo. of silk. The goods are worked for an hour, the bath is brought up to 95° C., 35 grammes of sulphate of copper are added, and the silk is left for 24 hours in the bath.

H. Lange (*F.Z.*, 1890, p. 359) gives the following process for dyeing wool and cotton mixtures; the goods are crabbed as usual and padded in a solution of

80 grammes aniline salt,
40 „ chlorate of potash,
20 „ sal ammoniac,
10 „ sulphate of copper,
10 „ British gum,
3 c.c. vanadate of ammonia, 1 gramme per
litre,
1 litre water.

The aniline salt is dissolved in 250 c.c. of water, the chlorate of potash and the sal ammoniac in 600 c.c., the dextrine and the sulphate of copper in 250 c.c. The hot solutions are mixed after cooling and the vanadate of ammonia is added immediately before use.

The British gum may be replaced by starch or gum tragacanth water.

If the material receives too heavy a nip in the padding machine the black comes out thin, and, on the other hand, if the pressure is insufficient it takes a brownish colour. On leaving the padding machine the goods are dried at 35° C., aged for 12 to 15 hours in hot, moist air, washed, chromed a quarter of an hour in 1 gramme bichromate of potash per litre, washed, soaped at 70° C. with 7 grammes of soap per litre, rinsed and dried. The goods may be shaded by adding logwood to the soap bath. For a very full black the chroming is done in a hotter and stronger bath.

Kayser and Schulz (*D.R.P.*, 61,087), in dyeing silk and cotton mixtures, reserve the silk by a hot mordanting with tannin. The silk thus treated is not dyed in the aniline bath. The silk may be freed from the tannin by a passage at the boil through an alkaline or acid bath and dyed in the ordinary manner, leaving the cotton black.

Kallab uses Lightfoot's process of chlorination for prussiate black. His process was patented by K. Oehler (*D.R.P.*, 68,887 and 71,729). The thoroughly degreased wool is treated for half an hour to an hour in a cold bath containing 6 to 10 per cent. of

the weight of chloride of lime and 9 to 15 per cent. of hydrochloric acid at 21 B. It is then washed and printed or dyed as follows:—

Padding Bath.

405	grammes	aniline salt,
150	,,	chlorate of soda,
260	,,	yellow prussiate of potash.

Bring up to 3,150 c.c. with water and add about 200 grammes of glycerine. This addition of glycerine is intended to preserve the handle of the wool and at the same time has the effect of giving a fuller black.

Printing Colour.

800	grammes	British gum water,
200	,,	aniline salt,
75	,,	chlorate of soda,
130	,,	yellow prussiate,
250	,,	water,
40	,,	tartaric acid.

It is not necessary to chrome this black. The printing colour may also be prepared by dissolving 22 grammes of chlorate of soda in 180 grammes of hot gum tragacanth, 125 grammes per litre, and adding cold,

81	grammes	aniline salt,
52	,,	yellow prussiate,
278	,,	water.

Kallab obtains a white or colour discharge on pure woollen cloth or a mixture of wool and cotton padded in the above bath.

White Discharge.

228	grammes	British gum water,
50	,,	glycerine,
300	,,	acetate of soda,
150	,,	zinc dust,
150	,,	bisulphite of soda, 34° B.

For colour discharges the following thickening is used, to which solutions of the colouring matters are added:

500	grammes	British gum water,
200	,,	acetate of soda,
100	,,	sulphocyanide of potassium.

For woollens, such colours are used as Brilliant Ponceau 6R, Tartrazine, Chinoline Yellow, Rhodamine B, Carmine Blue B, and Malachite Green. For gloria, silk and wool, colours for silk fast to washing are chosen. For wool and cotton mixtures direct

cotton colours dyeing the two fibres equally are used, or a mixture of these colours with acid colours for wool, with the addition of acetate and phosphate of soda.

The following printing colour is also recommended for wool previously oxidised by Kallab's process:

400	grammes	gum tragacanth	water, 50 grammes per litre.
1,550	„	water,	
150	„	glycerine,	
200	„	wheat starch,	
450	„	light British gum,	
150	„	chlorate of soda,	
200	„	red prussiate of potash,	
400	„	aniline salt.	

Steam for half an hour without pressure and rinse. To hide the yellow colour of the wool Kallab recommends that the chlored wool should be bleached with peroxide of hydrogen before padding, and that a small quantity of Acid Violet should be added to the white discharge.

Kallab gives the following directions for the mourning style on silk. The goods are padded with the following mixture:

4,000	grammes	aniline salt in 6 litres of water,
2,600	„	yellow prussiate in 15 litres of water,
1,500	„	chlorate of soda in 3 litres of water.

Dry carefully and print on the following discharge:

500	grammes	British gum	water 1 : 1,
400	„	acetate of soda,	
100	„	hyposulphite of soda.	

Heat and add without boiling

500 grammes wheat starch in powder.

Give two passages through the Mather and Platt or steam for 5 minutes and finish by washing with water.

Horace Koechlin recommends that the chlorinated wool should be padded in a bath of sulphate of aniline, 100 grammes per litre, and printed for the white discharge with thickened chloride of tin, 800 grammes per litre, then padded through bichromate of potash, 100 grammes per litre. According to Koechlin, the black develops in the cold on the non-reserved part.

Skawinski oxidises the wool before printing with 5 to 10 per cent. of its weight of persulphate of ammonia. He works with a very dilute aqueous solution. The goods remain in this for one or

two hours, they are then hydro-extracted and padded with

120	grammes	aniline salt,
45	„	chlorate of soda, and
80	„	yellow prussiate per litre of bath.

Steam for half an hour without pressure and wash. The fault of this process is that it is too expensive.

H. Koechlin obtained the Prud'homme style on half silk by using Grafton's process.

F. Reisz uses permanganate of potash as oxidant for the wool. The bistre which is deposited on the fibre also assists to develop the aniline black. The wool, to begin with, is treated in a bath of cold water to which from 3 to 4 per cent. of the weight of the wool of sulphuric acid, 66° B. is added, to neutralise the alkali remaining from the suint, and then 6 to 7½ per cent. of permanganate of potash is added to the same bath. The wool oxidised and dyed by the permanganate is padded or impregnated with a bath containing per litre of water

80 to 100	grammes	aniline salt,
28 to 34	„	chlorate of soda,
10 to 15	„	tartaric acid,
20 to 30	„	sal ammoniac,
30 to 40	„	sulphide of copper paste,
15 to 20	„	glycerine.

The goods are aired in the ageing room for 14 to 16 hours at 36 to 40 hygrometric degrees, then steamed for two minutes and soaped hot. In this process the oxidation is effected both by the manganic oxide deposited on the fibre and by the chlorate of soda.

J. Pokorny (*B.S.M.*, 1900, p. 112), basing his process on Oehler's patent (68,887), worked out a simpler method for wool and half wool, which he used in the print works of Kutteneberg. The union material is gassed, washed for half an hour at 45° C., soaped for an hour and three quarters at 45° C., with a kilo. of soap and 100 grammes of soda per litre, then passed through a fresh bath for half an hour at 45° C. with 100 grammes of soda. It is then washed in the washing machine, squeezed out and bleached at full width in peroxide of hydrogen, or for pure wool, bisulphite. The bleaching is done in a wooden vat heated by a lead steam pipe. The bath is brought to the boil, the steam shut off and 3 litres of silicate of soda and 48 litres of peroxide of hydrogen are added to the bath containing 170 litres. Six pieces are rapidly entered into this bath, which must cover them entirely, and stirred with a pole for three to four hours. The goods are then squeezed out, washed in rope form, squeezed again and chlorinated at full width in a pair of jiggers. The first jigger contains 120 litres of water, 9 litres of hydrochloric acid, 4° B., and 11 litres of chloride of

lime, 4° B. This mixture marks about 0.6 to 0.7° B. The second jigger contains fresh water.

The goods remain about 16 seconds in the first jigger, pass through the second at once, and are then washed in rope form. The bath in the first jigger is reinforced by the addition of the two solutions as required, that is to say, 9 litres of hydrochloric acid in 60 litres of water, and 11 litres of chloride of lime in 60 litres of water. The wool or half wool thus chlorinated and washed is then squeezed thoroughly and padded with the following solution for steam aniline black:—

3,000	grammes	aniline salt,
1,125	„	chlorate of soda,
11,950	„	yellow prussiate.

The bath is brought up to 20 litres with water. After dyeing the goods may be printed with the following colour discharge:—

30	grammes	colouring matter,
650	„	starch and light British gum thickening,
60	„	sulphocyanide of potassium,
380	„	zinc white 1: 1.

The colour discharges used in a similar case in cotton printing give good results; for instance, the colours containing zinc white, gum tragacanth and albumen. Either basic or acid colours are suitable.

The printed and dried material is then steamed for 15 minutes with a wet back cloth. It is then washed in cold water. Admitting that about 100 metres of woollen muslin weighs 7 kilos. it absorbs 10 litres of the chlorine bath made with 11 litres of chloride of lime, at 4° B., 9 litres of hydrochloric acid, 4° B., brought up to 120 or 140 litres with water. This corresponds to 7 grammes of dry chloride of lime and 20 grammes of hydrochloric acid, 21° B., per kilo. of material, or 0.7 per cent. of chloride of lime and 2 per cent. of hydrochloric acid of the weight of the wool. From this calculation it will be seen that a weak chlorination is sufficient.

Bethmann (*D.R.P.*, 130,309) takes the same view as Hommey that the formation of the black is prevented not only by the reducing properties of the wool, but also by its alkaline action. He recommends the treatment of the wool for half an hour at the boil with a sufficient quantity of water and 5 per cent. of the weight of the wool of sulphuric acid, or an equivalent quantity of hydrochloric acid, or a mixture of the two. The goods are then impregnated in the bath for aniline black, which contains 40 to 50 grammes of chlorate per litre more than the quantity necessary for the oxidation of the aniline. The wool, therefore, after having been squeezed or hydro-extracted retains 2 to 3 per cent. of its weight

of chlorate to counteract the reductive properties. The following example is given to the specification :

85	grammes	aniline oil,
25	,,	chloride of copper,
25	,,	sal ammoniac,
75	,,	chlorate of soda,
45	,,	acetic acid,
165	,,	hydrochloric acid, 16° B.

This is for one litre of padding bath. The black is developed by remaining for some hours in the hot ageing chamber. It is then chromed with 5 per cent. of bichrome, rinsed and soaped. If this black is printed on it may be also developed by steaming. The wool may also be prepared by adding the excess of chlorate to the acid bath. It is in this case treated at the boil for half an hour with 5 per cent. of its weight of sulphuric acid, to which 2 per cent of chlorate is added.

E. Reisz (*C.Z.*, 1903, p. 215) states that since September, 1899, he had used a process communicated to the Farbwerke vorm. Meister, Lucius and Brüning, in which he replaced the oxidation of the wool by an acid treatment. In his report to the Farbwerke he states that "acidified wool behaves like cotton in the presence of a bath for oxidation aniline black. The passage through sulphuric acid has the effect of preventing the production of easily sublimable (!) free aniline during the passage through the bath of aniline salts." According to Reisz this free aniline, together with the excess of chlorate, changes the conditions of the dyeing, and alters the structure of the wool. He describes also several interesting experiments in which he padded the goods through a bath richer in chlorate of soda and in acid than the ordinary bath for oxidation black, developed for fifteen hours at 36 to 40 hygrometric degrees, then steamed 1 to 2 minutes in steam mixed with air and ammonia at 75 to 80° C., and finished as usual. This process was carried out on the following cloths :

1. Wool freed from suint, without other treatment.
2. Wool freed from suint, boiled half an hour with 8 per cent. of sulphuric acid, rinsed and dried.
3. Wool freed from suint, boiled half an hour with 6 per cent hydrochloric acid, rinsed and dried.
4. Wool freed from suint, boiled half an hour with 16 per cent. of hydrochloric acid, rinsed and dried.

The results were as follow :

1. Hardly took the dye.
2. Gave a mediocre greyish black.
3. A dirty grey, the structure of the wool slightly altered.
4. A dirty grey, the wool was hardened and had lost its elasticity.

A series of similar experiments were made with a slightly modified steam black for cotton.

87	grammes	aniline oil,
87	„	hydrochloric acid 21 B.,
55	„	chlorate of soda,
190	c.c.	ferrocyanide of ammonium solution,
15	grammes	glycerine.

Pad on dry and steam 15 minutes without pressure.

1. Gave a grey, the others were completely stripped on soaping. Reisz concludes that "on acidified wool an oxidation black alone is available. Among the acids tried sulphuric acid is that which is most suitable and the preliminary treatment of the wool is not in itself sufficient to obtain a fine black, whereas this can be obtained by a more complete oxidation of the wool."

Reisz is of opinion that Bethmann's patented process, in which the acid bath also contains an oxidant, is the most advantageous. At the same time he recommends that the chlorate should be replaced by permanganate. This process has been tried on wool and cotton unions.

Jacquet was the first to solve the problem of applying the Prud'homme discharge style to aniline black on wool. He described the process in a document under seal deposited with the Mulhouse Society on August 8, 1891, and opened in 1903 (*B.S.M.*, 1903, p. 416).

Jacquet submits the wool to an energetic chlorination 25 per cent. stronger than usual and, in order the better to counter-balance the reductive properties of the animal fibre, he replaces the ferrocyanide of potassium by the ferricyanide. The following is the padding bath:

500	grammes	red prussiate,
500	„	chlorate of potash,
10	litres	water,
2,500	grammes	aniline salt
$\frac{1}{16}$	litre	vanadate of ammonia solution.

The solution of vanadate of ammonia is prepared with:

40	grammes	vanadate of ammonia,
$\frac{1}{2}$	litre	water,
320	grammes	glycerine,
160	c.c.	hydrochloric acid.

Bring up the whole to 4 litres.

The padded material is dried and printed with the following white discharge:

10	litres	egg albumen solution,
3,200	grammes	hyposulphite of soda,
3,200	„	acetate of soda,
10,000	„	zinc white.

Steam for 5 to 10 minutes at 100° C. in the Mather and Platt, run through hot water and dry.

Jacquet prepares colour reserves by adding sulphide of cadmium, red lake or Guignet's green to the above white discharge. H. Schmid (*B.S.M.*, 1902, p. 419) says that Jacquet's process gives a better and deeper black than that of Kallab, and, moreover, gives also a purer white. Schmid believes, nevertheless, that Kallab's process is the more suitable for colour discharges. For these he uses wool colours with the addition of acetate of soda, and these are preferable to the pigment colours used in Jacquet's process. He mentions Chinoline Yellow, Carmine Blue, and a mixture of Tartrazine and Carmine Blue for green.

Franz Konitzer (*B.F.*, 347,067, 1904) commences by fixing Prussian blue on the animal fibre, wool or silk, alone or in mixture cloths, then dyeing with any aniline black. The Prussian blue is produced by simply boiling the goods in an acidulated solution of ferricyanide of potassium in the usual way. Konitzer (*R.G.M.C.*, 1905, p. 309) gives a detailed description of his process which seems to be assured a great future success.

He states that the cost of dyeing one kilo. of pure cheviot wool is 0.68 by steaming and 0.77 to 0.79 francs by the bichromate process. Establishment charges are calculated in this at 25 per cent.

CHAPTER X.—Aniline Black on Mercerised Cotton and Artificial Silk.

Artificial silk and mercerised cotton are very similar in their properties from the point of view of dyeing. The current commercial artificial silks are:

1. Chardonnet and similar silks made from nitro-cellulose, among which are Beaulieu and Valette silks.

2. Viscose silk.

3. Cupra-ammonium silk, such as Givet, Glanzstoff and Linkmeyer silks. The silks of this class are very permeable to water. They absorb it easily, whereas untreated cotton is not wetted out with pure water, except with extreme difficulty.

The silks of the cupra-ammonium class can be dyed aniline black in the following manner: The silk is first thoroughly wetted out in hot water and the hanks are then worked for some time in a freshly-prepared cold bath made by mixing the three following solutions:

1,200 grammes	chlorate of soda,
12 litres	water.

2,160 grammes	ferrocyanide of potassium,
11 litres	water.

3,360 grammes	aniline salt crystals,
9 litres	water.

Hydro-extract, steam for a few minutes in the Mather and Platt, pass quickly through a $1\frac{1}{2}$ per cent. bath of bichromate of potash at 60° C., wash, hydro-extract and dry.

F. Beltzer (*M.S.*, 1907, p. 88, *D.C.P.*, 1907, 54 and 74) studied the subject closely, and we give the results of his research:

SINGLE BATH ANILINE BLACK.

Mercerised cotton, of course, requires a weaker dyebath than untreated cotton. With ordinary cotton a fine medium black can be dyed in the cold by using — per 100 kilos of goods:

7 litres	aniline oil,
$10\frac{1}{2}$ „	sulphuric acid, 66° B.,
50 „	water.

16,800 grammes	sodium bichromate,
50 litres	water.

Bring up the bath to 1,200 litres.

If the same weight of mercerised cotton is dyed in this bath a very deep bronzy black is obtained which it is almost impossible to convert to a pure black even by a prolonged soaping at the boil. If the baths are weakened, however, the same pure black is obtained.

5 litres aniline oil,
7 „ sulphuric acid 66° B.,
50 „ water.

12,000 grammes sodium bichromate,
50 litres water.

Bring up the bath to 1,200 litres.

The black on leaving the dyebath is bronzy, but a boiling soap bath soon changes it to a full pure black, which is even deeper than that obtained with 7 per cent. of aniline on ordinary cotton. To obtain a black on 100 kilos of mercerised cotton equal to the 7 per cent. black on ordinary cotton the following quantities are required:—

4 litres aniline oil,
5½ „ concentrated sulphuric acid,
50 „ water.

10,000 grammes sodium bichromate,
50 litres water.

The bath is brought up to 1,200 litres.

The bronzy black obtained turns to a full black of the same depth on soaping at the boil. The mercerisation is here supposed to have been done in the usual way for lustring, the fibres being kept stretched. If the cotton is allowed to shrink the bronzy black obtained with 4 per cent of aniline cannot be brought to a full pure black by soaping.

A fibre strongly mercerised, or to speak more correctly, treated with concentrated caustic lye, will have an absorbent power proportional to the amount of contraction. If a hank of cotton is mercerised without tension with caustic soda lye of 40° B. containing sulphide of carbon, or if, in other words, partial gelatinisation or a superficial transformation of the fibre into viscose is caused, a contraction occurs which continually increases until the superficial layer of viscose is dissolved. After three or four days' maceration in the liquid the yarn turns brown and shrinks and shrinks until it ends by being converted into viscose—a structureless, gelatinous mass. If, instead of pushing this action to extremity, only partial gelatinisation is reached, a much swollen and contracted hank is obtained, gelatinous in appearance, but with sufficient tenacity to enable it to be rinsed, bleached or dyed. When dyed in a single bath with 4 per cent. of aniline, according to the last recipe, it takes a bronzy black, which cannot

be altered by soaping. Three per cent. only of aniline must be used :

3	litres	aniline oil,
4 $\frac{1}{2}$	„	sulphuric acid, 66° B.,
50	„	water.

8,000	grammes	sodium bichromate,
50	litres	water.

A hank of Louisiana cotton yarn 0.68m. long before treatment shrinks to 0.20m. when converted into viscose. After rinsing, souring, bleaching, etc., it gives, with 3 per cent. of aniline, an excessively deep bronzy black, very difficult to convert to a full pure black by soaping. It is very difficult to dye level, even when the amount of acid in the bath is lessened so as to make the dye go on more slowly

With these experiments as a basis, Beltzer sought for the best method of dyeing viscose silk. With 3 per cent. of aniline a bronzy black only is obtained, and it cannot be changed to a pure black. By using weaker baths less bronzy blacks are obtained. These blacks green very readily, as might have been expected, as the proportion of aniline is too small to prevent it, even with an extra amount of bichromate. The black obtained even with 2 per cent. only of aniline is bronzy, and turns green under the weakest reducing action, and it is extremely difficult to get level dyeings. Other inconveniencies of this method of dyeing viscose silk are that the colour bleeds, and the silk loses its lustre as the molecular aggregates of colouring matter are so voluminous and opaque as to obstruct the transparency of the thread. The colour comes off on dry rubbing, as might have been expected.

Beltzer records that so far his attempts to dye aniline black on artificial silk or mercerised cotton in a single bath have given only a coppery bronze black, interesting in itself, but incapable of being converted into a full pure black. All attempts to get a deep black by lessening the amount of aniline have resulted in a black that so easily turns green as to be quite useless. The bronze can, of course, be obtained for its own sake, but it destroys the lustre of the thread and the handle.

Beltzer therefore turned his attention to oxidation black. The results are interesting, both from the point of view of the depth of the black and from the absence of harmful effect on the fibre.

OXIDATION BLACK.

When ordinary cotton is dyed with oxidation aniline black, it is generally more or less tendered, the tenacity being diminished by 15 to 25 per cent. In the case of mercerised cotton the loss is not more than 3 to 7 per cent. This represents the loss caused by dyeing minus the gain of tenacity conferred by mercerisation.

The loss of tenacity is not serious, and even when the upper limit of 7 per cent. is reached, it is impossible to say that the cotton is really tendered, for even in the raw state fibres show variations in tensile strength of 10 or even 15 per cent. Besides the increase in tensile strength given by mercerisation, the increased affinity for dyes must be taken into account; the employment of weaker baths diminishes the tendering caused by the dyeing.

The emeraldine develops on mercerised cotton and on artificial silk at much lower temperatures than on ordinary cotton, and much more rapidly. Thus, while a temperature of from 40 to 45° C. is required for oxidation on ordinary cotton, half the time at from 30 to 35° C. is sufficient for artificial silk. Complete oxidation on ordinary cotton takes from twelve to fifteen hours, and on artificial silk from eight to ten hours only. The emeraldine formed on artificial silk is darker than that formed on ordinary cotton; in fact, sometimes the black is developed.

The results with mercerised cotton are intermediate between those with ordinary cotton and with artificial silk. To develop the emeraldine completely as a dark green on a mercerised cotton requires from ten to twelve hours' oxidation at from 35 to 40° C., if the cotton has been mercerised under tension. If the cotton is allowed to contract, the oxidation does not take so long. The comparative tests were made with the same aniline bath in each case. It is evident that all the phenomena co-operate in lessening the chances of alteration of the fibre and the facility with which mercerised cotton and artificial silk are impregnated enables the manipulation necessary with ordinary cotton, which may have a prejudicial action, to be cut down to a minimum. Again, oxidation black dyeing is done in the cold bath, and this is another advantage, as hot baths and much manipulation cause entanglement, and consequent risk of breakage of the threads. In dyeing oxidation black the yarn is merely immersed in the bath and left quiet for fifteen minutes, or thirty at the most. It is then centrifuged and spread out in the oxidation room at a temperature of 35° C. at the maximum. When the emeraldine is developed the yarn is passed into the bichromate bath, left for another quarter or half an hour, rinsed in cold water, centrifuged and dried. Mercerised yarn thus dyed has a fine lustre, while the black is comparable to the best oxidation blacks on ordinary cotton, and there is no tendering. It is true that there is a slight loss of elasticity, but this occurs in all dyeing processes.

PROCESS AND APPARATUS.

The hanks are wrapped up loosely in lightly-woven natural silk in packets of from 2 to 3 kilos. The packets are placed carefully in the copper basket of a centrifugal, as shown in Fig. 17. In this *a* is the drum of the centrifugal, *b*, *b*¹ removable baskets, *c*, *c*¹ wooden vats placed below the centrifugal to receive the drainage from it, *g* driving axle of the centrifugal, *m* belt pulley driving

g, n gearing of g, k traveller working on the rail R to carry the baskets.

The basket, loaded evenly with the bundles of hanks, is lowered into the bath slowly and gradually, so as not to shift the bundles. No pressure is used. After half an hour's immersion the basket is lifted out, allowed to drain for a short time, and carried to the centrifugal by means of the traveller. Thus there is no handling to entangle the fibres. The centrifuged hanks are removed from the packets and laid on smooth boards of beech wood. Each board will take from 1 to $1\frac{1}{2}$ kilo. at the most of artificial silk. If the latter weight is exceeded the oxidation will be irregular. The boards are then placed in the oxidation chamber, which is heated by ribbed iron steam pipes, and is provided with a temperature regulator governing the steam inlet valve.

To treat 100 kilos. of artificial silk daily with convenience, the oxidation chamber must be 15m. \times 4m. \times 4m. Wooden chimneys provide a steady draught which will not cause sudden changes of temperature. At first the temperature may be allowed to rise to 40° C. without risk, but as the hanks dry it may be gradually brought down to 35° C., and towards the end the temperature

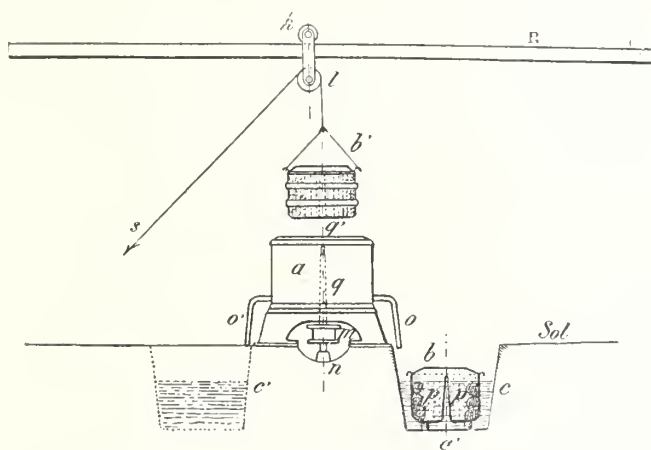


FIG. 17.—APPARATUS FOR DYEING ARTIFICIAL SILK.

should not exceed 30° C. During the oxidation the hanks must be turned to bring different parts of the yarn into contact with the wood, and in turning them they should be lightly shaken to separate the fibres which have clung together when wet. The hanks turn green gradually as they dry, and finally nearly black. When the oxidation is finished they have a uniform greenish black colour. There should be no trace of white or yellow even in the inside of the hank. The oxidation generally lasts one night. The oxidised hanks are again wrapped up loosely in natural silk as before, and the packages are placed in a basket kept specially for the purpose, which is then immersed in the bichromate bath. After from 15 to 30

minutes in this the basket is transferred to the centrifugal. After centrifuging the hanks are removed from the wrappings and rinsed in pure cold water, again centrifuged, and dried at about 30° C. This will take about two days, and the drying room should be 15m. \times 8m. \times 4m. It is heated by ribbed steam pipes, and the inlet valve is governed by a temperature regulator. The dry hanks are bundled in the usual way.

It will be seen that throughout all these operations the hanks are not handled wet; they are spread out on the boards after they leave the centrifugal. They are still damp, but there is little risk of tangling the fibres. Even this handling may be lessened if the hanks are wound to begin with on the special reels shown in Fig. 18. These are jointed so that they can be folded up for convenience in donning and doffing.

A is the profile of the wheel with its arms in their normal position, B the profile with the arms folded down, C front view of the wheel, a, a^1 , a^2 , very smooth and interchangeable laths of beech wood fixed at the ends of the steel arms, c^1 , c^2 , which are jointed to

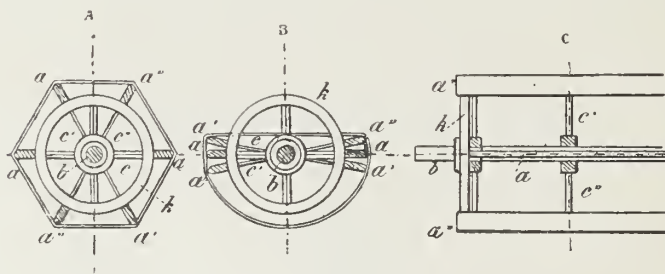


FIG. 18.—SPECIAL REELS FOR ARTIFICIAL SILK.

the axle b of the wheel and mounted on rings, c are fixed arms, and k the fixed steel circle serving as a guide to the movable laths.

The hanks are put on carefully and regularly so as to cover the laths completely. When this is done the wheel is brought to the normal position so as to stretch the hanks slightly. The hanks then undergo the whole of the operations on the reels and are not moved until the yarn is nearly dry in the oxidation room. The hanks must then be turned, and this is the only handling. When the emeraldine is well developed the reels are folded and the hanks are fixed on again. They are then chromed and rinsed on the reels. During the rinsing the reels are rotated slowly and the water circulates gently in the rinsing vat. When the rinse water no longer turns yellow the yarn is dried and centrifuged and the hanks are not removed from the reels until perfectly dry. The arms and the axle of the reel may be of steel or cast iron. The laths are interchangeable so that they can be replaced if they become warped or cracked.

The final drying is of special interest when a maximum lustre

is desired. It has long been known that the lustre of mercerised yarn is enhanced by drying under tension, or at least, better preserved, than if the hanks are dried loose. This is equally the case with artificial silk, as this also contracts on drying if dried without tension. The shrinkage makes the fibre, which is too transparent while wet, become opaque and, therefore, less brilliant. The reels described allow the hank to be dried under tension without any manipulation beyond that which is necessary to turn the hanks.

Fig. 19 shows a section of a drying room heated by ribbed steam pipes. In this, *t* is a pipe to admit steam to the ribbed radiators *T*, *c* is a steam valve governed by a Grouvelle and Arquembourg temperature regulator *R*, *h* thermometer, *EF* wooden

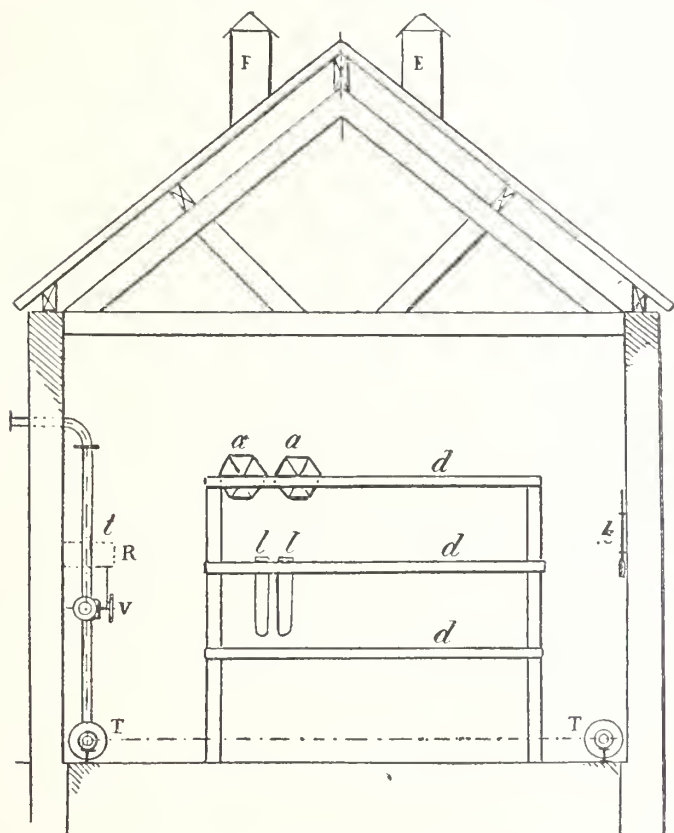


FIG. 19.—DRYING ROOM FOR ARTIFICIAL SILK.

chimneys, *l* drying laths for drying without tension, *a* jointed reels for drying with tension, and *d* wooden supports for the laths or reels. Both artificial silk and mercerised cotton are often finally gassed to increase the lustre.

The following recipe will give a slaty blue-black and a soft handle :—

5	litres	aniline oil,
6	„	hydrochloric acid 20° B.,
1	„	acetic acid,
5	„	glycerine,
33	„	soft water.

2,500	grammes	sodium chlorate,
2,500	„	sal ammoniac,
500	„	copper sulphate,
.005	„	ammonium vanadate,
5	litres	aluminium formiate, 20° B.

Make up to 50 litres with condense water.

The glycerine gives pronounced softness to the handle. By diminishing the glycerine and increasing the aniline the black is redder. The following formula may be adopted.

5½	litres	aniline oil,
6½	„	hydrochloric acid, 20° B.,
1	„	40 per cent. acetic acid.
1	„	glycerine,
36	„	soft water.

3,000	grammes	sodium chlorate,
500	„	copper sulphate,
.005	„	ammonium vanadate,
3,000	„	sal ammoniac,
2	litres	aluminium formiate, 20° B.

Make up to 50 litres with condense water.

When the two baths have cooled to about 20° C. they are mixed for use. If the yarn is to have a harder feel the glycerine must be omitted altogether, and the dyeing must not be followed by soaping; in fact, soaping should be avoided altogether as it gives a greasy feel and impairs the lustre. After chroming a thorough rinsing with cold water is sufficient.

To get a more bronzy, and at the same time deeper, shade, and to retain the suppleness and lustre, use the following bath :—

6	litres	aniline oil,
7	„	hydrochloric acid, 20° B.,
1	„	acetic acid,
2	„	glycerine,
34	„	water.

3,500	grammes	sodium chlorate,
700	„	copper sulphate,
.006	„	ammonium vanadate,
3,500	„	sal ammoniac,
750	„	ferric chloride, 30 to 35° B.

Make up to 50 litres with condense water.

Here the aluminium mordant is omitted as it tends to stiffen the fibre, and the glycerine is increased to give suppleness. The iron gives a reddish tinge, which is closer to a silk black. With this last formula the oxidation is very rapid and the black lustrous and deep.

By rapid centrifuging, 200 kilos. of goods can be impregnated with 100 litres of dyebath, or to put it in other words, after rapid centrifuging 100 kilos. will have absorbed only 50 litres of bath.

The black can be altered in depth by varying the proportion of iron and aniline. The glycerine is to give softness, but too much must not be used, as although the handle should be soft and supple, the yarn should possess some firmness. In all cases the handle must not be greasy, and it is therefore necessary to cut down the glycerine and to avoid soaping after dyeing. The aniline baths must be made with water as soft as possible (condense water), as lime salts injure the lustre by penetrating into the fibre. It is absolutely necessary that the mixture of the baths 1 and 2 be perfectly limpid. If any precipitate forms on mixing them, dissolve it by adding a little acetic acid or decant the bath from it or filter it off if necessary. To prevent the aniline bath from depositing sediment it must be stocked in an airy, dark place.

To prepare the bichromate bath dissolve sodium bichromate in twenty times its weight of cold water, or, better, potassium bichromate to the same strength. The potassium salt is dissolved in boiling water and diluted with cold. The bichromate bath must not be used for silk at a temperature exceeding 25° C. Bichromate of potash gives a deeper black than the soda salt. It is really $K_2Cr_2O_7$, but the commercial soda salt is never actually $Na_2Cr_2O_7$. In either case soft water should be used to dissolve the bichromate.

These processes are used for all the chief classes of artificial silk produced from cellulose. Beltzer (*D.C.P.*, 1907, p. 74) gives a large number of tables, showing the effect of oxidation black on the strength and elasticity of the various classes.

CHAPTER XI.—Aniline Black in Dyeing.

Lightfoot's method for the production of aniline black already described is more particularly adapted to textile printing, but nevertheless the inventor foresaw its extension to the dyeing of yarn and piece goods. As a matter of fact, his process, slightly, or not at all modified, is still used in many dyeworks.

BOBŒUF'S BLACK.

The first patent relating solely to dyeing is that of Bobœuf (*B.F.*, 68,079, July 15, 1865). This describes "The preparation and use of colouring matters capable of replacing black colours or blues such as indigo." The wording of the specification and the theories developed in it show, it is true, that the scientific requirements of the patentee left something to be desired, but it is no less true that by following his instructions exactly an excellent process of dyeing aniline black is realised. Bobœuf's method was not very successful at the time it was introduced, but this was because aniline and bichromate of potash were then too expensive. Aniline black, as everybody knows, had to compete with logwood black, which could be dyed at a very low price. Bobœuf's patent had a considerable influence on the development of aniline black dyeing, and it is necessary to give the main details of the specification at length. The process was only provisionally protected in England (*E.P.*, 1,947, 1865). The specification gives a very bare outline of it.

Bobœuf made use of the action of bichromate of potash on the salts of aniline, either on the ordinary salts or on what he calls the acid salts, which are simply the ordinary salts dissolved in an excess of acid. He thus obtained a colouring matter which he believed to be produced by double decomposition. As a matter of fact it results from the oxidising action of the chromic acid on aniline, the chromic acid itself resulting from the action of the free acid contained in the aniline salt on the bichromate. The double decomposition therefore occurs before the formation of the colour.

When neutral aniline salts and bichromate of potash are used, there is a brown colouration but no precipitate. If a precipitate were produced, immediately or slowly, it could not be used in dyeing. As a matter of fact, if sufficiently concentrated solutions of normal hydrochloride of aniline and of bichromate of potash are mixed there is a precipitate of bichromate of aniline. When under the same conditions, neutral chromate of potash is used, an oily yellow precipitate is formed, which is equally useless as a colouring matter. This is a mixture of bichromate of aniline and free aniline.

Bobœuf says in his specification: "If acid is first added to the

hydrochloride of aniline and this solution is poured into a solution of chromate or bichromate of potash, a blue or dark green precipitate is formed, having the appearance of intense black." And further on: "In dyeing silk, wool, or other animal substance, cotton, yarn, hemp, linen or other ligneous or vegetable substance, it is sufficient to pass the material into a salt or salts with which the salts of aniline can form precipitates or produce colours. For instance, pass the goods through a bath of chromate or bichromate of potash of the strength recognised as the best for dyeing without tendering the fibre, follow the ordinary practice before passing into the second bath and then steep the goods in a bath of hydrochloride of aniline. If desirable or necessary, the processes may be reversed, the goods may be passed through the hydrochloride of aniline bath and then through the chromate or bichromate of potash. The chromates, and notably the alkaline bichromates which produce blue colours with hydrochloride of aniline having after rinsing with water the appearance of the finest black, give dark green precipitates if these chromates are in excess."

Bobœuf also describes the precipitates which he obtained with other salts of aniline, such as the oxalates, the arseniates, and the ferro and ferri cyanides. "Each salt of aniline gives a black with a particular reflex. The yellow and red prussiates give light and dark blues and greens with the ordinary salts, and especially hydrochloride of aniline, whereas they give other shades with the other salts, and notably with the salts prepared with an excess of acid. From what has been said it will be understood that it is equally possible to dye goods or to obtain precipitates by pouring a neutral or ordinary salt of aniline into a salt (a chromate or bichromate, for instance) which this salt does not precipitate. Following up by rinsing in acidulated water or by adding acids to the mixed solutions."

In other words, the goods can be passed, to begin with, through bichromate of aniline and the aniline then oxidised by a passage through acid, or they may be dyed directly in a single bath with aniline salt, bichromate and an excess of acid, and this is the current process to-day.

Bobœuf's process in the hands of the dyers of the North of France, in Lille, Tourcoing, Roubaix, and other centres, has developed into a very simple and very economical method of dyeing. These dyers have kindly given us details of the current practice. Two separate solutions are prepared:

6,000	grammes	aniline dissolved in
9,000	„	hydrochloric acid,
12,000	„	sulphuric acid,
200	litres	water.

12,000	grammes	bichromate of soda,
200	litres	water.

Two litres of each of these solutions are put into a small earthenware mug and one kilo. of cotton is passed quickly through this bath.

The black develops in one or two minutes; it has a bronzy look. The goods are treated in this way a kilogramme at a time, then centrifuged, and steamed for a quarter of an hour at a quarter of an atmosphere pressure. The bronzy black is changed to a jet black, practically ungreenable. The goods are then washed and soaped.

The steaming process shows that the dyers of the North of France have profited by the research of the chemists, among others G. Witz (*B.S.R.*, 1874, p. 172), who noted that the black oxidised at a high temperature was less liable to turn green than that developed at a low temperature.

Alland (*B.F.*, 68,230, Aug. 5, 1865), a week or two after Bobœuf took out a similar patent. He works the goods, to begin with, in a solution of bichromate of potash, then in another strongly acidulated bath containing common salt and hydrochloride of aniline. By passing the textile material a certain number of times through these two baths a more or less deep black is obtained. The black deposit in the dyebaths can be collected on a filter and used as a pigment colour in textile printing.

Alfred Paraf (*B.F.*, 71,692, 1866, *E.P.*, 1,174, 1866) took out a patent in which he claimed the use of chromate of chrome (brown bioxide of chrome) to obtain aniline black either in printing or in dyeing. The principal points of the specification are as follow: "I prepare the textile fibre in a soluble salt of chromium, the chloride, for instance, then without washing I pass it into a solution of soda or other alkali, then into a neutral solution of a chromate of potash or of soda, and I wash, etc. In this way I precipitate on the fibre the insoluble brown bioxide of chrome, then I dye in a solution of a salt of aniline containing $2\frac{1}{2}$ per cent. of a chlorate. I squeeze out and allow to oxidise, then I treat in the same manner as for steam blacks."

At the end of his specification, Paraf makes the following claims:

1. The use of chromic acid as oxidising agent in printing in a single operation (operating under the conditions mentioned in this specification), using the insoluble or partially soluble salts of chromium capable of freeing chromic acid under the conditions indicated in this specification, as, for instance, the brown bioxide of chrome or chromate of chrome, chromate of the sesquioxide of iron, subchromate of lead, or, as more soluble salts, the chromate of chrome and of manganese, chromate of manganese, etc.

2. For the production of black with aniline or its analogues.

3. For the production of all colours produced in printing with chromic acid which so far have required two operations.

4. As mordants for reds, blues, or other madder colours, either alone or combined with the chlorate.

Paraf-Javal (*B.F.*, 69,254, 1865; *E.P.*, 3,110, 1865) describes "the manner of using the property of certain substances in order to obtain either new results or known results in a more advantageous manner." Paraf-Javal had noticed that many substances re-act too rapidly on each other to be used advantageously. For instance, chrome acid acts too rapidly on aniline or toluidine. He proposed to remedy this in dyeing, either by greatly increasing the volume of the bath containing chromic acid and the substance which generates the colour, aniline, for instance, and repeating the operation until the desired shade is obtained, or by neutralising the dyebath as far as possible, following by treatment in an acid bath, or, again, by refrigerating the bath sufficiently to retard the reaction. In this last case the goods take the colour immediately they are lifted from the bath.

The blacks and greys thus obtained by the action of chromic acid on aniline are, according to Paraf, different from those obtained by other processes. They are not turned green by acids and are insoluble in an essential or saponifiable oils and are also insoluble in aniline.

This process is on the same principle as that of Bobœuf, with the difference that Bobœuf speaks of the instantaneous production of the black in a single bath, which he doubtless used very concentrated, whereas Paraf-Javal dilutes his bath and allows the colour to develop slowly.

If Paraf-Javal's bath is heated at the end of the operation, and the utility of heating was pointed out in 1874, the process is exactly the same as that patented by Grawitz in 1877. We shall return to the process of Grawitz later.

Paraf-Javal (*E.P.*, 1,537, 1866) protects the following interesting process: "In the manufacture of aniline mauve, either by chromates, permanganates, or similar salts, there is a great quantity of black precipitate which has to be separated by washing from the mauve colouring matter. Not only this black is almost of no value, but the washing forms a very long operation. I overcome this by fixing in the fibres the chromate, permanganate or similar salts, and then by dyeing in a salt of aniline both black and mauve are fixed on the fibre. After dyeing I wash first in an alkaline water in order to separate it from the brown, then, by boiling in a high pressure apparatus (or bleaching pan, for instance) with alcoholised water I dissolve only the pure mauve and the black remains fixed on the fibre. In this matter through a simple operation I get at once a pure mauve, and a black which was lost before has served in this case to dye goods. I especially produce a cheap and fast mauve in this way of operating by using the oxide of manganese fixed on the fibre. I also use the manganese salt with advantage for the production of aniline black which remains on the cloth after the mauve has been taken out. I have also found that the more cool is a mixture of a salt of aniline and metal the less is it liable to decomposition, for

instance, when chromic acid is mixed with a salt of aniline it is almost decomposed at once into black, but if mixed in a vessel remaining in a freezing mixture it keeps undecomposed as long as the mixture is below zero. I have applied for this purpose the freezing machine of Mons. Carré, and in passing my cloth or yarn through a mixture of chromic acid and aniline salt, kept cold by one of these apparatus, the cloth remains of a lemon yellow colour, but whenever it comes out of this cold bath the fast black is found insoluble on the fibre."

Higgin (*E.P.*, 897, 1866) recommended that the goods should be prepared with an insoluble chromate, for instance, chromate of copper, and then printed or padded with aniline salt. The chromate of copper could be obtained by double decomposition, using neutral chromate of potash or soda, or chromate of copper could be used in solution in ammonia as the ammonia would be driven off on drying.

Carves and Thirault (*B.F.*, 73,345, 1866) claim "The use in dyeing and in printing of various greys soluble in boiling water, and resistant to acids and to soap, obtained directly from aniline and its homologues." They call these Mureines, and obtain them by the action of bichromate of potash, a salt of iron, and an acid on a solution of a salt of aniline in an excess of acid. Patterns of various grey dyeings obtained by this process were shown at the Paris Exposition of 1867.

Reimann (*W.J.*, 1867, p. 56) gives the following process for dyeing cotton: Treat with a soluble salt of the oxide of chrome, pass without washing through carbonate of soda, then through chromate of potash, so as to fix the insoluble chromate of chrome, dye in a solution of aniline salt with the addition of $2\frac{1}{2}$ per cent. of a soluble chromate, squeeze, allow to oxidise until a dark green colour appears, then finally pass through bichromate to develop the black.

Persoz recommends that the chromate of lead should be fixed on the fibre to begin with, and that the goods should then be dyed in a sufficiently acid bath of aniline salt.

ANILINE BLACK OVER MANGANESE BISTRE.

C. Lauth (*B.F.*, 85,554, 1868; *E.P.*, 1,421, 1869) proposes to commence by fixing the oxide of manganese on the fibre, then to pass the goods through an acid solution of aniline salt. He mordants the vegetable fibres by the methods long since used in producing manganese bistre. As mordants for the animal fibres he uses alkaline manganates and permanganates. The dyebath contains per litre of water 50 grammes of aniline and 100 grammes of hydrochloric acid. "The concentration of the mordants and that of the dyebath, the nature of the acid and that of the alkaloid, aniline, toluidine, cumidine, naphthylamine, etc., vary according to circumstances and according to the nature of the desired black, which can be varied from a grey blue and a violet brown to the

most intense jet black. By modifying this process, that is to say, by mixing peroxide of manganese, a neutral salt of aniline and sal ammoniac, or any other agent capable of decomposing the peroxide of manganese under the influence of heat, then printing this colour and steaming, the black is also developed. The sesquioxide and the bi-oxide of manganese can be replaced by other oxides, or metallic acids rich in oxygen, as, for instance, plumbic acid (peroxide of lead), or by certain salts, such as the manganates or permanganates of barium and copper, or by chlorides of lead. It will therefore be seen that as a mordant I prefer insoluble bodies rich in oxygen or in chlorine, and capable of being very easily decomposed, and thus able to develop the aniline black by simple contact with an acid solution of aniline. The advantage of the insolubility of these mordants is that they can be combined easily with the articles to be dyed, and that their insolubility prevents them from being spread throughout the dyebath, thus causing the formation of the black in the bath itself instead of developing it on the fibre, which is the fault of the processes hitherto published."

In the completed specification six months later the patentee adds: "On leaving the bath I wash the goods in running water until all acid is eliminated, for a reason which will be readily understood, as everybody knows that aniline black turns green in the presence of acids. After this washing all that remains to be done is to dry the dyed goods, but the shade thus obtained can be modified at will by a sort of brightening or supplementary oxidation. This can be done by passing the yarn or piece goods through a lukewarm or boiling solution, the nature and concentration of which I determine according to the shade and the intensity of tone which is required. A very large number of salts is available for this purpose, among others, chloride of lime, or salts of chromium, copper, iron, and mercury, alone or together with chlorate of potassium, or ferricyanide of potassium and the chromates."

In a highly interesting article (*M.S.*, 1873, p. 794) Lauth gives more complete details of his process, and particularly insists on the necessity of the after treatment. "After dyeing the shades obtained can be modified or intensified by means of various agents. This fact seemed to me to be curious; it seemed to indicate that at the moment when the bioxide of manganese had terminated its action the colouring matter produced, and possessing all the properties of the black, is nevertheless still in an intermediate state, and that a further oxidation is useful to bring it to its definite state. Bichromate of potash, one gramme per litre, salts of copper, chromium, or of mercury, and especially a mixture of chlorate of potash, a copper salt and sal ammoniac, one gramme of each per litre, very considerably increases the intensity of the black. This bath should follow the washing after dyeing, and be given for half an hour at the boil. It should be followed by wash-

ing with water and a hot soaping. This process gives most beautiful and absolutely fast blacks, and does not tender the fibre."

Lauth's black becomes ungreenable by after treatment with chromate or hypochlorite of lime, and it is ungreenable without this after treatment if the goods are dyed in the acid bath of aniline salt at a higher temperature than 75° C. If the dyeing is done in the cold bath and the goods are then steamed, as in Bobœuf's modified process, already described, the blacks do not green appreciably. Lauth's process was not as successful as it merited, but it has been taken up since, not exactly for dyeing yarn or piece goods, but on a large scale for topping discharged manganese brown with aniline or naphthylamine.

Gonin, of Rouen, in 1870 or 1871 worked a process, of which he also sold the rights to several dyers. He passed the cotton through the two following baths:

1,000 grammes	hydrochloric of aniline,
1,000 ,,	hydrochloric acid,
600 ,,	chloride of copper crystals,
600 ,,	chlorate of potash,
500 ,,	sulphuric acid,
80 litres	water.

1,000 grammes	bichromate of potash,
500 ,,	sulphuric acid,
80 litres	water.

The two baths were reinforced with solutions prepared in the same way. This process was not made public at the time.

Persoz (*M.S.*, 1871, p. 396) succeeded in producing the black in a practical manner by modifying Paraf-Javal's process. He used the bichrome and the aniline salt in separate baths. He padded the goods through a solution of one of these salts and sprayed on the other at once in powder. According to his directions various acids may be employed in order to modify, according to requirements, the content of the solution in salts and the degree of acidity. He recommends a mixture of hydrochloric and sulphuric acids. The temperature can be regulated so as to dye immediately or to retard the reaction so that the black is not developed until the goods have circulated through a hot chamber. This can be arranged so that the goods are white on entering the apparatus and black when they leave it.

Persoz states that this same method, with slight modifications in the nature of the substances used, allows woollen to be dyed under advantageous conditions.

Alland, in 1871, modified his process already described. He passed the goods through a mixture of chloride of iron, aniline salt and chlorate of potash, then slowly heated them in a closed keir in such a way that the temperature remains for five hours

between 40° and 50° C. The goods are treated again in the same bath, and at the end of an hour they are finished by passing for 15 minutes through an acid bath of bichromate, rinsing thoroughly, treating with a solution of soda, and finally washing at the boil. This process accidentally came into the possession of L. Jarosson and Muller Pack, who patented it in France, with some insignificant modifications. (*B.F.*, 95,512, 1872, *E.P.*, 1,710, 1872) A!-land claimed priority and was allowed royalties by the patentees.

Nahrath and Firmenich, of Geneva, from the commencement of the year 1873 allowed their customers to use the following process: The goods are passed through a short bath of hydrochloride of aniline solution and tartaric acid, squeezed, and passed through a bath containing bichromate and hydrochloric acid. They are oxidised in this bath for several hours, then passed once more into the dyebath. This alternative treatment is continued until the black is sufficiently intense.

Tantin and Briere (*B.F.*, 101,685, 1874) propose to dye in a very acid single bath containing a salt of aniline and bioxide of manganese. They work with cotton in this for three hours. It has then taken a very dark green colour, and is finally oxidised in a bichromate bath.

R. Pinkney (*B.F.*, 102,050, 1874, see *E.P.*, 2,745, 1871) uses the salts of vanadium and of uranium in dyeing and printing. The advantages of vanadium had already been pointed out by Lightfoot in 1871. Pinkney recommends a one-bath process of dyeing; 150 grammes of hydrochloride of aniline, $\frac{1}{8}$ gramme of vanadate, 20 grammes of chloride of nickel, 100 grammes of chlorate of potash, and $2\frac{1}{2}$ litres of water. The goods are passed through this bath or may be treated to begin with, in a bath containing the metallic salts, and then into another containing the aniline salt and the chlorate. The dyeing may be done at the ordinary temperature, but in the majority of cases a higher temperature is more advantageous.

Although it has not been published, a process may be noted, invented by L. Bretonniere, of Laval, and sold on June 27, 1873, to J. J. Muller Pack. One litre of light aniline oil is dissolved in 2 kilos. of hydrochloric acid, 22° B., and 10 litres of hot water; and 1,200 grammes of bichromate of potash in 10 litres of hot water. For 10 kilos. of cotton yarn, 2 litres of the aniline solution are put into a tub containing 90 litres of water at 60° C. The yarn is entered and worked for ten minutes, then 2 litres of the bichromate solution are added. The yarn is again worked for ten minutes and takes a grey colouration. Another 2 litres of the aniline solution are put in, the yarn is worked ten minutes, then 2 litres of the bichromate solution are added, and so on until the two solutions are used up. The yarn is then a bronzy black, from 200 to 300 c.c. of the hydrochloric acid is added to the bath, the yarn is worked in this for five minutes, lifted and squeezed, then washed in plenty of water, acidulated with sulphuric acid and finally

rinsed, or sometimes a soaping follows the rinsing. This process gives a very fine and ungreenable black.

De Vinant dyes cotton yarn by passing it through a solution of sulphate of copper acidulated with hydrochloric acid, then through a bath of sulphate of sodium, then through a solution of sal ammoniac, chlorate of potash, and pyrolignite of aniline, and finishes with a bath of bichromate of potash. It is evident that the yarn should be stretched between the two last baths.

Lamy (*W.J.*, 1874, p. 100) showed that aniline black is much more resistant and much less liable to turn green when it has been super-oxidised. The reddish black, obtained by a passage of the dyed goods through bichromate and then through a bath of hypochlorite of sodium, is much faster to washing and to acids than the bluish black obtained by a passage through a soda bath.

STRIPPING ANILINE BLACK.

G. Witz (*B.S.R.*, 1874, p. 100) states that printed or dyed aniline black can be stripped by passing the goods first through an acid solution of permanganate of potash, then through oxalic acid. "When a pattern of aniline black, even chromed, and whether or not first turned green by sulphurous acid, is steeped in sulphuric acid 9° B., with the addition of a small quantity of a cold saturated solution of permanganate of potash crystals, the decolouration of the black is noted after a few minutes. The green tint is gradually hidden by the brown deposit of oxide of manganese. If then steeped in an acid solution, particularly oxalic acid, the cotton takes a beautiful white, if the printed black was not too intense, and the fibre is only moderately tendered. By treating alternatively with the permanganate solution and the oxalic acid, in fine powder or in solution, the aniline black can be stripped completely or in particular places in order to remedy defects in the dyeing. Tartaric acid has less action than oxalic acid.

Depierre notes that a mixture of bichromate of potash and oxalic acid has a similar effect on aniline black. A cold aqueous solution of pure chloric acid acts in a similar way, the aniline black turns green and is then stripped.

W. J. S. Grawitz, as we have already seen, took out his first patent on September 30, 1874 (*E.P.*, 3,632, 1874). Although the specification merely applies to textile printing and to the preparation of aniline black in powder it eventually became a hindrance to the French dyers. Grawitz took out a certificate of addition to this patent on October 3, 1874, and two other patents on November 3 of the same year. These can be referred to in a previous chapter.

Coquillion (*B.F.*, 106,031, 1875) describes several processes of preparing aniline black based on the action of the salts of iron on the salts of aniline in the presence of a chlorate. As an example he gives the following dyeing process:

For 20 kilos. of wetted out cotton take 3 kilos. of aniline and 4

kilos. of hydrochloric acid, 20° B. Mix the two liquids and allow them to cool. Then add 2 kilos. of chlorate of potash dissolved in 30 to 35 litres of water, mix thoroughly, and finally add 35 litres of proto-chloride of iron, 20° B., and bring up with sufficient water to work the yarn. Enter the cotton into this mixture and leave it 8 to 12 hours at the ordinary temperature. Then lift and steep in a solution of carbonate of soda, 10 to 15° B., in order to eliminate the excess of acid. Rinse, enter the cotton into a bath of bichromate of potash heated to about 50° C., and containing about 200 grammes of bichromate dissolved in 30 to 35 litres of water. This bath gives the black more resistance, and prevents greening. The cotton may be left in it about half an hour. Then wash, squeeze and pass into a final softening bath, containing 500 grammes of Turkey red oil and 1 kilo. of carbonate of potash or soda per 30 to 35 litres of water.

Grawitz took out a second certificate of addition to his first French patent on April 29th, 1875.

Leriche (*B.F.*, 109,193, 1875) dyes cotton by alternate passages, first through a hot mixture of chlorate and bichromate of potash solutions, then through a hot solution of sulphate of aniline. The passages through these baths are repeated several times.

Ladureau in 1875 proposes to impregnate the cotton with a solution of chloride of maganese, chloride of iron, chlorate of potash, and of aniline salt, to allow it to age for 24 hours, and to pass without rinsing through a bath containing about one per cent. of potash to develop the black completely. The bichrome bath may be cold, but acts better when it is heated.

L. Wagner (*W.J.*, 1875, p. 992) took out a Bavarian patent for a method of obtaining a dark blue on yarn or piece goods. He thickens half a litre of glucose solution with 40 grammes of starch, and adds 40 grammes of chlorate of potash. In another half litre of glucose solution he dissolves 80 grammes of hydrochloride and 13 grammes of sulphate of aniline. Finally in 2 litres of the same solution, 40 grammes of chloride of copper, and 13 grammes of sulphate of copper. After mixing the three solutions the cotton is entered, wrung, allowed to remain in a heap for an hour, then oxidised for four to five hours in a moist chamber at about 30° C. it is then passed through dilute milk of lime, then through diluted hydrochloric acid, and finally through carbonate of soda or soap. The glucose retards the oxidation of the aniline, and prevents the development going beyond a dark blue.

Antony Guyard (Hugo Tamm) (*B.S.C.P.*, 1876, p. 58) has published an interesting article on the part played by vanadium in the formation of the black. We have already referred to this in a previous chapter. He says among other things that aniline black is simply dehydrated emeraldine; that a high temperature is necessary in the oxidation chambers, not in order to form the emeraldine, but to dehydrate it and to transform it into black; that the emeraldine can be dehydrated even in the liquid in which it is

formed by heating the bath, and it is then transformed into aniline black, just as the hydrated oxide of copper, which is blue, is transformed by boiling into the anhydrous oxide of copper, which is black. Guyard gives later a very simple method of differentiating emeraldine from aniline black. The former is completely dissolved and destroyed by hydrosulphide of ammonia, whereas aniline black is hardly affected by this reagent.

Witz (*B.S.R.*, March, 1876) contradicted this. He says that an emeraldine produced in the cold bath, that is to say, at a temperature below 18° C., is not hydrated, and is as insoluble in hydrosulphide of ammonia as aniline black itself.

Jeannolle (*B.F.*, 112,132, 1876) patents a method of obtaining a dark blue to replace economically blue tints obtained with pure indigo. For 100 kilos of cotton he takes 1,600 litres of water, 5 kilos. of hydrochloric acid, 12 kilos. of sulphuric acid, 5 kilos. of aniline, and 5 kilos. of bichromate of potash. The goods are dyed in the cold bath for an hour, then washed, and the last traces of acid are neutralised in a slightly alkaline bath at 40° C. The dyeings thus obtained are topped with an aniline blue or with indigo.

Hommeys later in the same year (*B.S.R.*, 1876, p. 263) described the following process:—The dyebath is prepared with 1,000 grammes of water, 80 grammes of hydrochloride of aniline, 40 grammes of chlorate of potash, 5 grammes of hydrochloric acid, and one tenth of a gramme of vanadate of ammonia. The colour is developed by ageing, and the black is finished by a passage through a hot solution of bichromate of potash.

Gouillon in the *Moniteur de la Teinture* of July 5th, 1876, states that a high temperature must be used at some step of the process in order to produce a well-fixed aniline black with no tendency to turn green. The heat may be applied by ageing in a chamber at 40 to 50° C., but this is liable to tender the fibre, and it is preferable to pass the cotton through a boiling solution of bichromate of potash after oxidation.

Grawitz took out the first certificate of addition to his second French patent on August 24th, 1876. He recapitulates the chemical reactions which he had patented for the production of black and other shades with aniline, and the processes which he claimed, but omits in this recapitulation everything he recognised as being inexact and unpractical in these processes, taking the opportunity to improve his patents by profiting by the progress realised in the meantime by other inventors.

PREVENTING GREENING.

John Bryson Orr (*E.P.*, 3,731, 1876) describes a method of preventing greening of aniline black. The printed pieces are passed after ageing through a boiling bath of about 2 per cent. of bichromate of potash, to which a little acid is added. This treatment should last at least a minute. The pieces are then soaped at the

boil, dried, and then passed into a cold bath containing chlorate of aluminium or another chlorate, such as chlorate of ammonia. The bath should contain one part of the salt to 600 parts of water. The goods are again dried and steamed for about half an hour. If the goods are boiled for half an hour to an hour in the chlorate bath the steaming is unnecessary; in this case the chlorate bath should contain one part of the salt to 100 parts of water.

Orr adds that the bichromate bath can be used for several batches, and that the goods should be steamed as soon as possible after the drying that follows the chlorate bath. This treatment not only prevents greening, but improves the black and gives a purer white. The same process is used for dyed goods, but in this case a weaker chlorate bath is used.

Grawitz took out his fourth French patent, 115,160, on October 21, 1876, for dyeing and printing ungreenable aniline black.

Theilig and Klaus (*D.R.P.*, 9,804, 1880), of Krimmitschau, dye the cotton yarn or piece goods in a cold bath with hydrochloride of aniline with the addition of chlorate of potash or another oxidant and chloride of vanadium. The goods are squeezed or centrifuged, and put into a closed apparatus where they are submitted to a current of hot air, which is mixed with steam as soon as they are sufficiently dry. In this way the oxidation of the aniline is rapid and complete, and the acid vapours are driven off. The goods are then passed into a bath of bichromate of potash or an alkaline bath. They are then rinsed, and if necessary softened with soap or oil, then topped with aniline colours and dried.

Theilig and Klaus inform us that they still work this process, and that it is in use in a number of other dyeworks.

Gilliard, Monnet and Cartier, at Saint Fons, to obtain ungreenable aniline black use a mixture of hydrochloride of paraphenylene diamine, hydrochloride of aniline, an alkaline chlorate and vanadium. The mixture of the two hydrochlorides is known as Monnet's Salt; 7 kilos. of this is dissolved in 50 litres of water, and 12 litres of Monnet's Mordant, that is to say, the chlorate and vanadium, is also brought up to 50 litres. Two litres of each of these solutions are mixed in an earthenware vessel, and one kilo. of the cotton is entered and squeezed so as to leave 1 litre of the liquid in the cotton. For the second kilo. of cotton the bath is reinforced with only half a litre of each solution and so on until it is exhausted. The cotton is then aged for 8 to 9 days, and turned once each day. The oxidation is then complete and the goods are washed and dried.

In dyeing cotton piece goods concentrated solutions of the salt and of the mordant are used. The pieces are padded, left rolled up for 24 hours, washed, chromed and soaped. The soaping may be dispensed with.

As we have already noted the processes for the production of aniline black may be applied to other bases. Ortho-toluidine gives

a violet black; a dark brown violet is obtained with alpha-naphthylamine; a brown with beta-naphthylamine; a dark brown with para-phenylenediamine; a yellowish brown with benzidine. The application of these bases has not been very successful. The puce obtained with alpha-naphthylamine has been given up on account of the disagreeable odour of this base.

Lehne (*F.Z.*, 1890, p. 332) gives the following process for dyeing cotton, silk and cotton, and ramie. The dyeings obtained are ungreenable, or very nearly so. They do not rub and do not sensibly tender the fibre:

400 grammes	starch,
5 litres	water,
600 grammes	chlorate of soda, dissolved in
3 litres	water,
100 grammes	sulphide of copper,
1,000	„ aniline salt, dissolved in
2 litres	water,

The whole is thoroughly well mixed and passed through a fine sieve into an earthenware vessel. The cotton is passed two or three times through this mixture, hank by hank; after each passage it is wrung and well equalised. It is then hung up in a moist chamber for one or two days at a temperature of 30° C. The yarn should be well opened and often turned, so as to obtain as regular an oxidation as possible. On leaving the ageing room it is passed for ten minutes through a bath at 80° C., containing

60 grammes	bichromate of potash,
40	„ sulphuric acid, 66° B,
100 litres	water,

It is then washed thoroughly in cold water, then passed for 15 minutes through a bath at 70° C., containing 100 grammes of olive oil soap, and 60 grammes of carbonate of soda per 100 litres of water. Then rinsed with cold water and dried at a moderate heat.

Lehne attributes to the starch paste the property of preventing a too rapid formation of the black on the fibre, thus avoiding bleeding. That this view is correct may be proved by leaving the starch out of the above formula; the black will then bleed. Instead of ageing the goods may be steamed for an hour and finished as above. The black has the same good properties, but the fibre is tendered.

The vertical and horizontal drying and ageing frames for yarn in the hank shown in the illustrations are the specialities of C. G. Haubold, junr., of Chemnitz. The construction will be readily understood from the diagrams, and the method of getting the necessary tension on the hanks is obvious. In the vertical machine there are twelve arms on a central axis, and these carry twelve

wooden frames. In each of these there are three pairs of bars to receive three rows of hanks. Each frame carries $1\frac{1}{2}$ kilos. of yarn per pair of bars so that the apparatus can treat 54 kilos of yarn at a time which with 25 or 30 turns of the machine requires about half an hour to dry. It takes half an hour to load the machine. The horizontal machine has eight fixed and eight movable bars mounted as shown. Each pair carry about $2\frac{1}{2}$ kilos. of yarn, so that the machine can treat 20 kilos. at a time which in 130 to 150 turns dry in half an hour. It takes a quarter of an hour to load the machine.

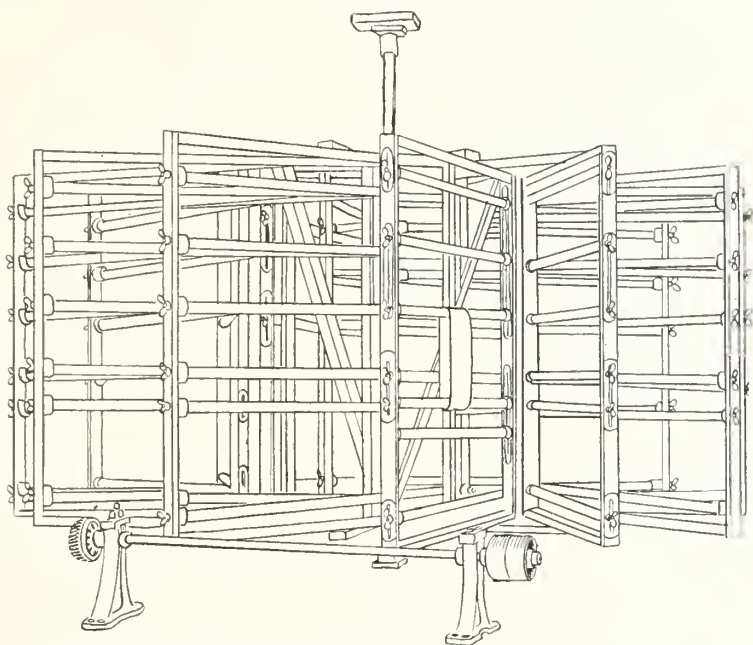


FIG. 20.—HAUBOLD'S VERTICAL DRYING AND AGEING FRAME FOR YARN.

E. Weiler (*F.Z.*, 1890, p. 162) describes the following simplified processes for a cheap black on cotton yarn:—

1. Pass 10 kilos. of cotton into a bath of 500 grammes aniline, 1,500 grammes of hydrochloric acid, 21° B, and 1,000 grammes of bichromate of soda. Work from an hour and a half to two hours until the black develops, then wash and dry.

2. Pass 10 kilos. of lightly soaped yarn into a cold bath containing 800 grammes of aniline, 3,200 grammes hydrochloric acid 21° B, and 1,600 grammes of bichromate of potash. Work for half an hour, heat the bath slowly, so as to reach the boiling point in two hours, and boil for a quarter of an hour. The slow increase of temperature makes the black go on very regularly; the bath exhausts better, and the colour is fuller.

These two processes give a brownish black, and are only used for warps, in goods that are to be parti-coloured, and must be very

fast to washing. The warps are usually slashed through rather acid size, and this improves the tone of the black.

For brighter blacks Weiler recommends No. 1, passed through

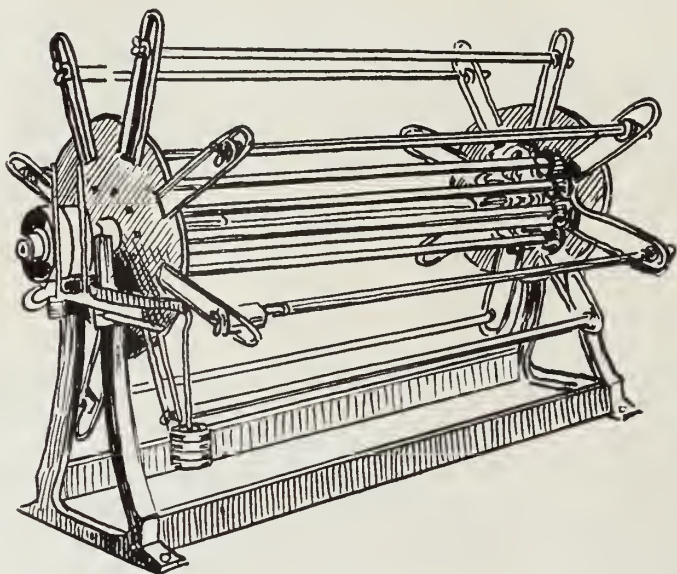


FIG. 21.—HAUBOLD'S HORIZONTAL DRYING AND AGEING FRAME FOR YARN.

a soda bath, then treated with sulphate of iron and finally brightened with logwood extract.

Under the initials E.P., the *Oesterreichs Wollen und Leinenindustrie*, of 1891, p. 515, makes the following notes on aniline black dyeing. According to E.P. the essential constituents of an "aniline mordant" should be reduced to the following elements in the stated relative proportions: 100 parts of aniline, 85 to 90 parts of hydrochloric acid at 21° B, 40 parts of chlorate of potash, and 2 parts of sulphate of copper. Any other addition is of secondary interest. Sal ammoniac, which is usually added in quantity equal to the chlorate, preserves a certain degree of humidity during oxidation; the addition of British gum allows even shades to be produced on yarn. There is no practical utility in adding anything else to the bath, glycerine among other things giving no particular advantage. The treatment after dyeing must be regulated according to the shade desired. The following processes may be used:—

1. Treatment in a very weak solution of carbonate of soda, 80 grammes of soda ash per 100 litres of water. The temperature may be varied.
2. Treatment in soap and soda, 80 grammes of soda ash and 50 grammes of soap per 100 litres of water.
3. Treatment with 40 grammes of bichromate of potash and 40 grammes of soda per 100 litres of water at various temperatures.

4. Passage for a few minutes through a bath containing 40 grammes of bichromate of potash and 10 grammes of concentrated sulphuric acid per 100 litres of water, followed by a thorough washing and soaping lightly, or better still, oiling in a cold bath with the addition of soap.

Each of these treatments and the temperature at which it is effected has an influence on the shade and the fastness of the black. The dyer therefore must learn by experience which treatment is best under given circumstances.

Justin Mueller (*F.Z.*, 1893, p. 17) recommends the use of chlorate of copper in dyeing aniline black on yarn. In two litres of water dissolve 350 grammes of sal ammoniac and 600 grammes of commercial chlorate of copper, 20° B. Make another solution of 480 grammes of aniline salt in 1 litre of water. Mix the two solutions, pass the yarn two or three times through the mixture, brought down to 4° B by the addition of water, and age for 12 to 24 hours in moist air, at 25 to 30° C. The yarn should then be green. Pass again through the same bath, age a second time, and chrome for half an hour at 40° C., with 4 kilos. of bichromate of soda per 50 kilos. of yarn, wash and soap.

Thies and Cleff (*D.R.P.*, 57,467) have patented the use of fluoride of aniline, which tenders the fibre less than the other salts of aniline in general, and the hydrochloride in particular. The Farbenfabriken vorm. Fr. Bayer and Co., point out the following method of use:—

Dissolve in a wooden vessel:

6,000 grammes	fluoride of aniline,
500 ,,	nitrate of copper,
10 litres	cold water.

Make a paste separately with:

600 grammes	starch,
1,200 ,,	chlorate of potash,
25 litres	water.

Boil and stir up until the paste is cold, then mix the two and bring up to 50 litres.

After dyeing, dry at 40 to 50° C., and oxidise at 50° C. Then pass for ten minutes through a bath at 80° C. containing:

60 grammes	bichromate of potash,
50 ,,	sulphuric acid, 66° B,
100 litres	water.

Wash thoroughly. The fluoride has the serious inconvenience of attacking the hands of the workmen.

Soxhlet (*F.Z.*, 1891, p. 200) describes a process for a one-bath aniline black on yarn in the hank. A cold bath of aniline salt, bichromate and sulphuric acid is made in a wooden beck. The yarn is entered as soon as the mixture is prepared and worked for

some time. It is passed after rinsing through a bath containing 10 litres of pyrolignite of iron, 12° B, and 100 grammes of bisulphite of soda, 40° B, per 100 litres of water.

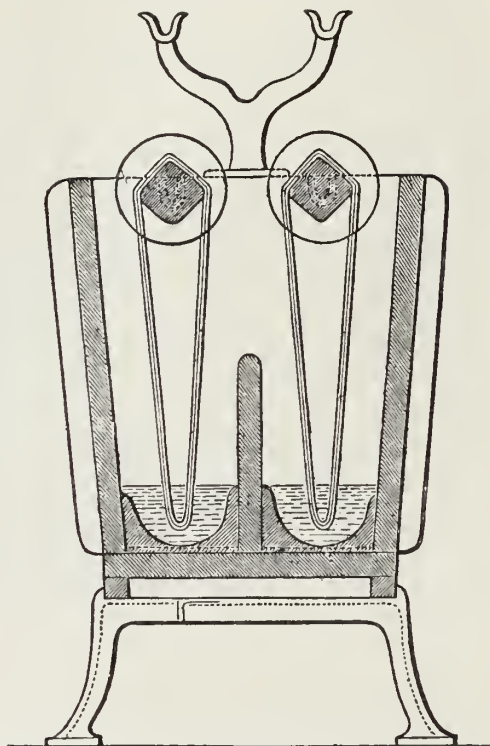


FIG. 22.—APPARATUS FOR DYEING YARN IN SHORT BATHS.

E. Weiler (*F.Z.*, 1893, p. 64) describes an improvement on this process. For 10 kilos. of cotton prepare a bath with:

900	grammes	aniline,
1,200	„	sulphuric acid,
1,200	„	bichromate of soda,
300	„	nitrate of iron, 30° B.

Enter cold, raise the temperature to 72° C, rinse and prepare a second bath with:

1,500	grammes	sulphate of soda,
500	„	carbonate of soda,
200	„	Diamine Black BO.

Work the yarn in this for one hour at the boil and give four turns in a cold bath slightly acidulated with sulphuric acid. Diamine Black BO gives bluish tones, and the BH mark gives still bluer tones.

Jagenburg (*B.F.*, 220,031, 1892) avoids the use of the chlorates

which tender the fibre and obtain an ungreenable black by passing the cotton through a bath of :

250	grammes	aniline salt,
300	„	acetate of copper, 12° B,
1,750	„	water,
15 to 30	„	acetic acid,

This bath is used at 25 to 30° C. The yarn is left for three or four days, and then passed through a bath at 40° C. containing :

1,500	grammes	water,
4	„	bichromate of soda,
4	„	chlorate of potash.

The yarn is oxidised for 1 to 6 hours.

C. Steiner (*D.R.P.*, 73,667) dyes the piece goods or yarn after mordanting in ferro- or ferricyanide of copper. This is done by passing the goods through a bath of sulphate of copper, 28 to 30 grammes per litre, then through a bath of prussiate of potash, 15

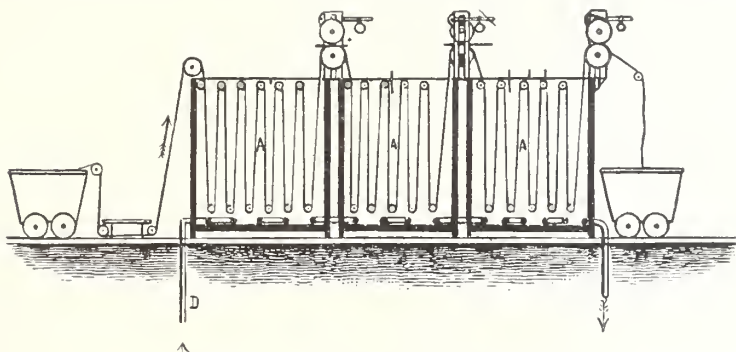


FIG. 23.—CONTINUOUS DYEING MACHINE.

to 30 grammes per litre. The goods thus mordanted are passed through a bath containing aniline salt, chlorate of soda, and prussiate of soda. They are then dried at a temperature of 40° C., at the maximum, and steamed at a pressure of not more than an atmosphere.

C. H. Boehringer Sons (*D.R.P.*, 96,600) replaces the hydrochloride of aniline by the lactate in order to avoid tendering the fibre.

120	grammes	hydrochloride of aniline in
600	c.c.	of water,
30	grammes	nitrate of copper in
300	c.c.	of water.
100	grammes	chlorate of soda in
450	c.c.	of water,
90	grammes	sal ammoniac in
300	c.c.	of water.

To each 300 c.c. of this mixture 30 c.c. of lactate of aluminium is

added. This is prepared with 100 grammes of sulphate of alumina dissolved in 200 c.c. of water decomposed by 175 grammes of lactate of barium dissolved in 300 c.c. of water.

The 120 grammes of aniline salts in the above formula can be replaced by a mixture of 60 grammes of hydrochloride, and 85 grammes of lactate of aniline. 1 kilo of cotton is entered into an earthenware vessel containing 4 litres of bath, after dyeing it is dried at 25° C., and developed for four hours at 50° C. in an atmosphere saturated with moisture. The goods are then chromed for 24 hours (!) in a bath containing 50 grammes of bichromate of potash per 8 litres of water.

To render this black fast to acids it must be passed through a fresh bath containing 3 per cent. of bichromate, 1 per cent. of aniline salt, $\frac{1}{2}$ per cent. of toluidine salt, 2 per cent. of lactic acid, and $1\frac{1}{2}$ per cent. of sulphuric acid. Enter cold, let the goods remain in the cold bath for an hour, then raise the temperature to 80° C., and give another hour.

According to these instructions the aniline does not seem to be sufficiently oxidised.

The Farbwerke vorm. Meister, Lucius and Brüning recommend Dianil CR as a bottom for aniline black on yarn. The goods are thoroughly wetted out and dyed at the boil with Dianil Black CR, and then in the following bath for 50 kilos of cotton.

1,750 grammes	aniline salt,
1,175	„ sulphuric acid,
750	„ sulphate of copper,
2,500	„ bichromate of potash,
800 to 1,000 litres	water.

Work in the cold bath for half an hour, adding the bichromate to it in small quantities, raise the temperature in half an hour to 60° C., and work for another half hour at this temperature.

METHYLATED SPIRITS IN COP DYEING.

Marot and Bonnet (*B.F.*, 271,703, and 275,169) add methylated spirits to the bath for aniline black. This gives better penetration and allows the cotton to be dyed without wetting out. Moreover, the reductive properties of the alcohol preserve the cotton from tendering. As a rule one-fifth of the bath is replaced by spirits of wine. The process is specially used for knitting yarns. The patentees use it on a large scale at Troyes for dyeing millinery goods.

L'Huiller (*B.F.*, 288,188) uses methylated spirits in dyeing cops and spools in his patented apparatus. The yarn is packed in a holder over a perforated plate, a vacuum is produced, and the yarn is impregnated with the bath for aniline black. The excess liquor is then driven off by allowing the air to re-enter and by suction. The cops are oxidised by blowing in hot air at 60 to 70°

C., treated with chromate at 40° C., raising the temperature to 80° C., washed, soaped and dried with hot air. Clement Marot at Troyes has used L'Huillier's apparatus since 1902, and by its aid has obtained an oxidation aniline black on spools and cops in the way in which it is produced on yarn or piece goods. The fibre is impregnated with a solution of aniline salts and an oxidant, then oxidised at the desired temperature and fixed as usual with bichromate. It is difficult in practice to impregnate cops thoroughly by the ordinary means of dyeing oxidation black, as a regular and penetrating oxidation necessitates that the yarn should be thoroughly dry throughout the cop. Baths of unusual concentration must therefore be used, and the great difficulty with these is that a precipitate is rapidly formed which prevents them from being worked in the ordinary manner. This is prevented by the use of methylated spirits; the alcohol retards the reaction in such a manner that the bath remains clear and without precipitate throughout the process. As we have stated, the use of spirits of wine also allows the cops to be dyed without being previously wetted out, and this saves a large amount of time.

The method of oxidation of the cops has also been modified; whereas in treatment in the hot chamber the cops are oxidised from the outside inwards, Marot oxidises from the interior to the exterior by blowing a current of hot air through the cop by means of a perforated nickel tube. When the oxidation proceeds from the exterior to the middle of the cop, there is no possibility of watching the progress of the oxidation, which is very slow, and almost always tenders the fibre, whereas by adopting Marot's method the emeraldine does not appear on the outside of the cop until the yarn is oxidised throughout, and this does not take more than 12 to 15 minutes.

Moreover, the current of hot air frees the fibre from the dangerous volatile products, such as the chlorine compounds which are formed during oxidation. The chroming is done as usual, and experience has shown that this after treatment may be put off for several hours after dyeing, so that the gaseous acid can be completely eliminated. Marot notes that cops are dyed much more cheaply than hanks with aniline black.

Kopp, Noelting and Grandmougin (*B.S.M.*, 1894, p. 382) reported on a new process of dyeing aniline black over manganese bistre to the Mulhouse Society. The bistre is produced by the reducing action of tannin on permanganate of potash. The cotton is tanned at 60° C., with 60 grammes of tannin per litre of water, or by giving two passages through the padding machine in 100 grammes of tannin per litre. The goods are then passed through a solution of 30 grammes of permanganate per litre of water, washed and dyed in an acid bath of aniline salt. This process can be applied also to mixtures of silk and cotton. The reporters, however state that it is not to be recommended either as regards price or results.

SUMMARY OF METHODS ACTUALLY IN USE.

Beltzer (*R.G.M.C.*, 1902, pp. 59, 95, and 111) gives a summary of the methods of dyeing actually in use. They may be divided into two principal groups:

1. Dyeing in one bath.
2. Dyeing by development in oxidation apparatus.

In the one bath processes of dyeing a large number of salts has been proposed to fix the black as thoroughly as possible, but as a rule in practice Bobœuf's bath is used; that is to say, the aniline is employed in the state of hydrochloride or sulphate, with the addition of bichromate of soda as oxidant.

The bath may be either hot or cold. For a hot one-bath black, Beltzer recommends the following:—

Rich Black.

8,000 grammes	aniline oil.
32,000 ,,	hydrochloric acid,
2,000 ,,	sulphuric acid,
50 litres	water.
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12,580 grammes	bichromate of soda,
50 litres	water.

The bath is brought up to 1,400 litres, the two solutions being added at once or in two portions.

Medium Black.

6,000 grammes	aniline oil,
20,000 ,,	hydrochloric acid,
10,000 ,,	sulphuric acid,
50 litres	water.
<hr/>	
12,000 grammes	bichromate of soda,
50 litres	water.

Bring up to 1,400 litres and dye as above.

Cheap Black.

4,000 grammes	aniline oil,
30,000 ,,	hydrochloric acid,
50 litres	water.
<hr/>	
8,000 grammes	bichromate of soda,
50 litres	water.

Bring up the bath to 1,000 litres.

A sufficiently large wooden beck is used. The quantities above are in each case for 100 kilos. of cotton. For each 50 kilos. of cotton 12,500 grammes of the bichromate solution is poured into the bath. The goods are given a few turns, $12\frac{1}{2}$ litres of the aniline salt solution is added, and the goods are worked for half

an hour. The second portion of the solution of bichromate and of aniline salt are then added, the goods are worked for half an hour in the cold bath, and then steam is slowly turned on, until the cotton takes a dark green colour, the bath is then quickly brought up to 60 to 70° C., and the goods remain in it at this temperature for a quarter of an hour. The dyeing operation thus takes about 2 hours.

When the dyebath is properly made up it should contain neither aniline salt nor bichromate after the goods are lifted. This can be easily tested by taking a little of the bath, adding some bichromate, and boiling it, which will precipitate the aniline salt in the state of aniline black, and by making a second test for excess of bichromate with acetate of lead. In case either the aniline or the bichromate is in excess, the correction is made in making up the bath for the next batch until the exact proportion is hit upon.

Beltzer gives the following recipes for dyeing in the cold bath. In each case the bath is for 100 kilos. of cotton.

Rich Black.

9,220 grammes	aniline oil,
24,800 ,,	sulphuric acid, 66° B,
50 litres	water.

21,600 grammes	bichromate of soda,
50 litres	water.

The bath is made up to 1,200 litres, the solutions are added in two portions.

Medium Black.

7 litres	aniline oil,
10,500 grammes	sulphuric acid,
50 litres	water.

16,800 grammes	bichromate of soda,
50 litres	water.

Make up to 1,200 litres, and add the two solutions at once.

Ordinary Black.

6 litres	aniline oil,
9 ,,	sulphuric acid,
50 ,,	water.

14,400 grammes	bichromate of soda,
50 litres	water.

Make up the bath to 1,200 litres, and add the two solutions at once.

Dye in the same manner as in using the hot bath. Work to

begin with in the bichromate solution, then add the aniline salt solution and work the cotton for an hour and a half.

Beltzer made a series of experiments to determine the best method of producing a single bath aniline black.

1. 6 litres water,
 500 c.c. sulphate of aniline, representing 30 c.c. of
 aniline, and 45 c.c. sulphuric acid, 66° B.,
 1,000 c.c. bichromate of soda, representing 72 grammes
 of bichromate of soda (64.1 per cent.),
 46.184 grammes, Cr O_3 .
2. 6 litres water,
 500 c.c. sulphate of aniline, as above,
 1,000 „ bichromate of soda, as above,
 25 grammes sulphuric acid.
3. 6 litres water,
 500 c.c. sulphate of aniline, as above,
 1,000 „ bichromate of soda, representing 72 grammes
 of bichromate (70.3 per cent.), 50.6
 grammes Cr O_3 ,
 24 grammes sulphuric acid.
4. 6 litres water,
 500 c.c. sulphate of aniline,
 1,000 „ bichromate of soda as in No. 3.

No. 2 bath develops most rapidly; No. 4 is the slowest in development. At the end of three hours the four baths are exhausted, both as regards aniline and chromic acid. The blacks obtained with Nos. 2 and 3 seem weaker and more violet than those with Nos. 1 and 4. In each case about 37 per cent. of the chrome used is extracted from the bath. Nos. 2 and 3 showed an abundant precipitant of aniline black.

Nos. 1 and 4 give the best results; an excess of acid as in Nos. 2 and 3 too greatly accelerates the development of the black. No. 1 is the best of the four.

One bath aniline black has two serious faults. It has a bronzy appearance, and a lack of resistance to rubbing; both these faults are remedied by soaping.

The oxidation process necessitates the use of two baths and the development of the black as far as the state of emeraldine after the first bath. The work is therefore more complicated, and moreover there is a risk of tendering the fibre, but the black is absolutely fast to rubbing, and the shade is fine and full.

The goods to begin with are impregnated in a bath containing aniline salt, a chlorate, and a metallic salt to act as an oxygen carrier. Beltzer calls this bath "emeraldinogene."

- | | | |
|----|---------------|-------------------------|
| 1. | 6 litres | aniline oil, |
| | 6 „ | hydrochloric acid 22 B. |
| | 1,000 grammes | tartaric acid, |
| | 47 litres | water. |
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- | | | |
|--|---------------|---------------------|
| | 2,000 grammes | chlorate of potash, |
| | 1,350 „ | sulphate of copper, |
| | 1,350 „ | sal ammoniac, |
| | 35 litres | water. |

The two solutions are mixed, the cotton is worked in them regularly to develop the emeraldine, and the goods are then chromed with 50 grammes of bichromate of soda per litre.

- | | | |
|----|---------------|--------------------|
| 2. | 10 litres | aniline oil, |
| | 10 „ | hydrochloric acid, |
| | 1,000 grammes | tartaric acid, |
| | 40 litres | water. |
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- | | | |
|--|---------------|---------------------|
| | 1,500 grammes | chlorate of soda, |
| | 1,350 „ | sulphate of copper, |
| | 2,000 „ | sal ammoniac, |
| | 58 litres | water. |

The treatment is as for No. 1, but 60 grammes of bichromate of soda per litre is used.

- | | | |
|----|---------------|--------------------|
| 3. | 2.4 litres | aniline oil, |
| | 2.4 „ | hydrochloric acid, |
| | 1,100 grammes | tartaric acid, |
| | 1,200 „ | British gum, |
| | 400 „ | glycerine, |
| | 8,000 „ | water. |
-
- | | | |
|--|-------------|---------------------|
| | 350 grammes | chlorate of potash, |
| | 270 „ | sulphate of copper, |
| | 400 „ | sal ammoniac, |
| | 6,000 „ | water, |
| | 1,800 „ | British gum, |
| | 600 „ | glycerine. |

Develop and finish as for No. 1.

The development of the emeraldine, as we have seen, should be watched with care, in order to avoid tendering the fibre. Beltzer says that the temperature in the drying chamber should not pass 50 to 60° C., and that there must be an energetic ventilation to carry away the harmful vapours. The temperature must not be allowed to fall below 40° C., as in this case the emeraldine will form too slowly and irregularly. For yarn special drying rooms

are used, in which the hanks are hung. Knittings are treated in the Preibisch apparatus.

Beltzer made a series of methodical trials to determine the degree of tendering of the cotton in the various processes of dyeing aniline black.

These experiments show that hydrochloride of aniline can be advantageously replaced by the borate, phosphate and tartrate.

Borotartrate of Aniline Black.

100 c.c.	aniline oil,
50	„ boric acid,
50	„ tartaric acid,
60	„ glycerine,
500	„ water.
<hr/>	
20 grammes	acetate of copper,
20	„ sal ammoniac,
20	„ chlorate of ammonia,
50	„ tartaric acid,
500 c.c.	water.

The 100 c.c. of aniline is dissolved in a hot bath of the indicated quantities of boric and tartaric acids. The two solutions are mixed at from 20 to 40° C., at which temperature the precipitated borate of copper redissolves.

The cotton is worked in this bath and dried in a moist atmosphere at 70° C. for about 6 hours, then passed through the bichromate bath. A higher temperature than 70° C. endangers the fibre, owing to the gases given off. For this reason Beltzer replaces one part of the chlorate by peroxide of sodium.

- | | | | |
|-------|----|---------------|----------------------|
| 1. | A. | 6 litres | aniline oil, |
| | | 3 | „ hydrochloric acid, |
| | | 3,000 grammes | arsenic acid, |
| | | 50 litres | water. |
| <hr/> | | | |
| | B. | 6 litres | hydrochloric acid, |
| | | 2,000 grammes | peroxide of sodium, |
| | | 50 litres | water. |
| <hr/> | | | |
| | C. | 1,000 grammes | acetate of copper, |
| | | 1,500 | „ chlorate of soda, |
| | | 1,000 | „ sal ammoniac, |
| | | 25 litres | water. |

B and C are mixed, and A is added. Dye and dry at 30 to 40° C., pass into the bichromate bath when the emeraldine is well developed.

2.	A.	100 c.c.	aniline oil,
		50 grammes	boric acid,
		50 „	tartaric acid,
		60 c.c.	glycerine,
		300 „	water.
<hr/>			
	B.	20 grammes	peroxide of sodium,
		60 „	hydrochloric acid,
		300 „	water.
<hr/>			
	C.	20 grammes	sulphate of copper,
		15 „	chlorate of soda,
		20 „	sal ammoniac,
		300 „	water.

Work as for No. 1.

3.	A.	150 c.c.	aniline oil,
		150 „	hydrochloric acid,
		700 „	acetate of alumina, 14° B.
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	B.	10 grammes	sulphate of nickel,
		5 „	sulphate of copper,
		20 „	chlorate of soda,
		20 „	sal ammoniac.

Mix A and B at as low a temperature as possible, and dissolve in :

300 grammes	peroxide of sodium,
90 c.c.	hydrochloric acid,

brought up to 1 litre with water.

Beltzer, by using peroxide of sodium avoids tendering the fibre, and obtains a fine black, but it is regrettable that the black develops very rapidly in the baths prepared with peroxide.

Beltzer considers acetate of copper to be the best oxygen carrier in dyeing oxidation black. It does not attack the fibre during the drying process.

In the manual describing the use of their colours the Farbwerke vorm. Meister, Lucius and Bruning give a recipe for an oxidation aniline black. At 10° B. this contains, per litre.

120 grammes	aniline salt,
40 „	chlorate of soda,
150 „	acetate of alumina, 14° B.,
5.7 „	sal ammoniac,
3 „	sulphate of copper.

The bath is brought down to 8° B., and the goods are impregnated with it, keeping up the strength of the bath by means of additions

of the 10° B. solution. The goods are wrung, equalised, dried and oxidised. They are treated for half an hour at 60° C. in a bath of 2½ per cent. of bichromate of potash, ½ per cent. of aniline salt, and 0.2 per cent. of sulphuric acid at 66° B., then thoroughly rinsed and soaped.

OXIDATION CHAMBERS.

The oxidation chambers play an important part in aniline black dyeing. According to a pamphlet by K. V. Kallab, published by K. Oehler, of Offenbach, any hot air drying chamber will serve for this purpose as long as it is well ventilated. A ventilating fan should be mounted in the roof of the chamber to suck out the air which enters the chamber from underneath the floor. The air openings lead into a large channel heated by steam radiators. The air entering the chamber is thus brought to the necessary temperature. It passes over the stretched-out cotton, and becomes saturated with moisture, then with the acid vapours formed later in the process, which would tender the cotton, and is finally expelled by the ventilating fan.

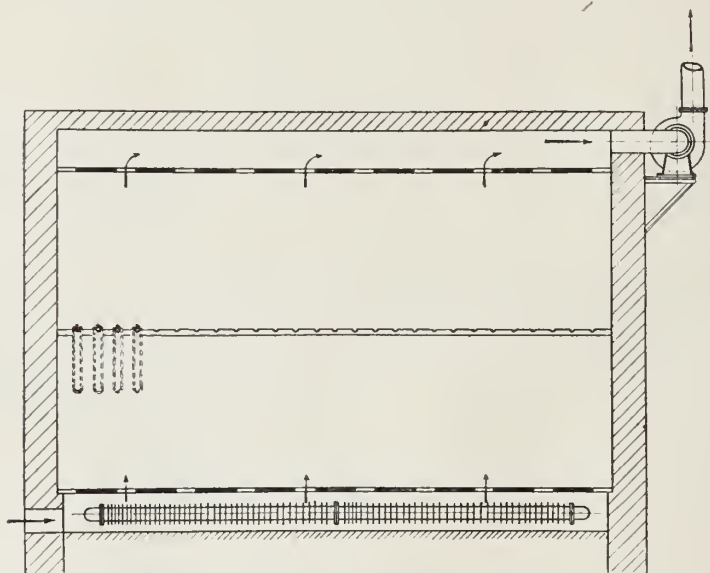


FIG. 24.—KALLAB'S OXIDATION CHAMBER.

The dimensions of the oxidising chamber naturally depend upon the daily output, but it is preferable to have too large than too small a chamber. For a batch of 100 kilos of cotton the chamber should contain 80 to 100 cubic metres. It must not be too low, a height of 4½ metres or thereabouts is suitable for working facilities. Under the roof a free space of from 1½ to 2 metres should be reserved. In this space the saturated air collects, and is drawn out gradually by the ventilator, as otherwise a current of air would cause inequalities in the dyeing. Also to prevent

a draught a false bottom should be provided within the chamber.

The temperature should be as uniform as possible in all parts of the oxidising chamber, and for this purpose the walls can be lined with boarding. If the chamber is sufficiently sheltered, all that is required is to coat the walls with boiled linseed oil, in order to preserve them from the action of the acid vapours, and also to prevent particles of mortar from falling on the goods.

The hanks are stretched in the usual way on rods, and the progress of the oxidation can be watched through a window at the side about 45 centimetres square, near which is placed a hygrometer. This apparatus consists of two similar thermometers fixed side by side. The mercury bulb of one of them is wrapped in cotton, which is kept constantly humid by means of a tube filled with water. The water in evaporating absorbs heat, and thus lowers the temperature of the wet bulb thermometer. The drier the air in the chamber the more active is this evaporation, and the greater the difference of temperature marked by the two thermometers.

The yarn is wetted out in water with the addition of 3 to 5 per cent. of carbonate of soda, rinsed and wrung on the wringing post, or hydro-extracted. It should retain as little water as possible and should be well opened out. It is then entered in quantities of 15 to 25 kilos. at the most at a time into the "mordant for black."

60,000 grammes	Oehler's Aniline Salt in
320 litres	of water,
2,750 grammes	sulphate of copper in
50 litres	of water,
18,800 grammes	chlorate of soda in
37 litres	of water,
2,000 grammes	sal ammoniac in
12 litres	of water,
24 ,,	acetate of alumina, 10° B.

A wooden beek holding about 600 litres is used, so that 25 kilos. of cotton can be easily worked at a time. The solutions are allowed to cool and poured into this one by one. The total volume is about 500 litres. The liquid marks 8° B. at a temperature of 15° C., and 7.5° B. at 25° C. The level of the bath should then be marked on the side of the beek.

The yarn is entered and worked for a quarter of an hour, lifted, lightly wrung, and placed in a hydro-extractor which should be near at hand, and the yarn must not be too energetically centrifuged. The operation must be regulated in such a manner that the cotton is double its original weight. It is equalised on the wringing post, and the mordant should be distributed as evenly as possible. The excess liquor from the hydro-extractor runs back into the beek, which is facilitated by its arrangement above the level of the bath.

The cotton is then put on the sticks. These are ordinarily of beech wood, and the precaution must be taken to rub them with the mordants and allow them to dry, otherwise where the wood comes into contact with the cotton it will absorb some of the mordant, and these places will show as light streaks.

The yarn is stretched very regularly and without tangling the threads. The ventilator is then set in action and the chamber is heated to 33° C. On entering the chamber the yarn is a dirty white. After drying it takes a light green, then a dark green. At the end of two hours the hanks must be turned. This is easier if instead of the ordinary round sticks, square sticks with rounded edges are used. The sticks should be thoroughly smoothed with glass-paper. Each stick, three metres in length, holds about 2 kilos. of cotton. The hanks are turned until what was previously the bottom of the hank becomes the top. Two workmen can turn 50 kilos. of cotton in eight to ten minutes. The work requires four men if the chamber contains 100 kilos. of yarn, as they should remain in the disagreeable atmosphere of the chamber as short a time as possible.

As we have noted, the drying and the oxidation are done in one and the same machine. Two hours after the first turn the hanks are turned again, but this time only half a turn is given. This operation is usually repeated every two hours. The cotton is dry four to six hours after it enters the chamber. The oxidation is then proceeded with at a humid heat. Steam is carefully introduced so that the dry bulb thermometer marks 35° C., and the wet bulb thermometer 30° C. Aniline black is then formed in its first state of emeraldine and gives off strongly smelling gases, consisting principally of hydrochloric acid and various compounds of chlorine and oxygen.

The yarn is treated until a greenish black colour appears; this is at the end of four to six hours, and sometimes longer. It is then taken out of the chamber and passed through the chromate bath. For 50 kilos. of cotton the following bath is used:

7,000 grammes	bichromate,
$\frac{3}{4}$ litre	sulphuric acid,
1,000 „	water.

Heat to 75 to 80° C., enter the cotton quickly and work ten to fifteen minutes. Then rinse thoroughly and soap with three grammes olive oil soap and one gramme carbonate of soda per litre of water at 80° C. for a quarter of an hour, rinse and finish.

As stated, the dyebath is for 25 kilos. at a time. When 100 kilos. have to be dyed the work is arranged so that they can be treated continuously in four batches. After the first batch the bath is somewhat diluted by the water contained in the cotton. It falls from 8 to about 7° B. Moreover, 20 to 22 litres of it are absorbed. The exact amount is ascertained by the mark on the

side of the beck. Every part of the cotton must, of course, be impregnated with the bath in the same degree of concentration. The bath, therefore, is reinforced by replacing the 20 litres absorbed by the cotton, that is to say, one-twenty-fifth of the 500 litres, by the corresponding proportion of the dyewares, that is to say:—

3,000 grammes	aniline salt,	
138	„	sulphate of copper,
940	„	chlorate of soda,
100	„	sal ammoniac,
1,200 c.c.		acetate of alumina.

These ingredients are dissolved in as little water as possible, about 10 litres, and poured into the beck. The bath is tested with the hydrometer and, if necessary, carefully diluted with water until it marks 8° B. When the dyer becomes expert by practice, he is able to simplify the operation by preparing solutions of aniline salt in its own weight of water, sulphate of copper, chlorate of soda, and sal ammoniac, using special measures representing a determined quantity of the salts dissolved. When the first batch is lifted from the bath and centrifuged, the indicated proportions of the various solutions are poured into the bath, the acetate of alumina is added, the degree is ascertained with the hydrometer, and the next batch is entered. In this way the bath is always kept in the same state of concentration. When it has been left standing and becomes turbid, or prolonged working leads to the same result, it must be filtered, otherwise the black on the goods will be somewhat dusty.

If the work is not to be continued only the quantity of bath necessary for the goods is prepared. The cotton is dried after wetting out and rinsing, and for 100 kilos. of cotton about a quarter of the quantity given above is prepared, that is to say:—

15,000 grammes	aniline salt,	
688	„	sulphate of copper,
4,700	„	chlorate of soda,
500	„	sal ammoniac,
6 litres		acetate of alumina.

This makes 125 litres of bath at 8° B. From 10 to 12 litres of this bath is put into an earthenware vessel, the cotton is preg-nated kilo. by kilo., the bath being kept up to strength with the prepared solution. The liquid must impregnate every part of the cotton. It is then lightly wrung three times on the wringing post and put in a heap, and when the 100 kilos. have been finished the operation is recommenced.

It is then centrifuged, the hanks are opened out and treated as above in the oxidation chamber.

No wooden utensil used in the dyeing of aniline black should be employed for any other purpose. The least trace of alkali produces a white spot, a drop of water makes a grey spot if it falls on the mordanted cotton.

The temperature, both in the drying operation and in the oxidation process should be kept within the indicated limits as if there is too much heat the cotton will be tendered.

The entry of daylight, and especially of the direct rays of the sun, must be avoided in the oxidation chamber.

When the black is to be particularly intense, a stronger mordant is used. A very rich, deep black is obtained with a bath at 8.5 to 9° B.

Fine counts of yarn require a stronger bath than the lower counts.

There must be the greatest possible regularity in all the operations, impregnation, hydro-extraction, drying and oxidising.

Mercerised cotton is dyed in a bath from 20 to 25 per cent. weaker than for ordinary cotton.

The exact shade of the finished black depends upon that of the emeraldine when it leaves the oxidation chamber; the work must be so regulated that the goods can be sampled in the daylight, that is to say, the actual process of dyeing should commence in the early morning.

C. E. Wild (*D.R.P.*, 118,174) has patented a process of dyeing an ungreenable black which has not the least tendering effect on the fibre, and is applicable to cotton, wool and silk. He impregnates these fibres in the following bath:—

15,000	grammes	aniline salt,
1,000	„	aniline oil,
3,000	„	acetic acid,
5,500	„	common salt,
7,000	„	chlorate of ammonia,
150	litres	water.

15,000	grammes	sulphate of copper,
5,500	„	acetate of copper,
150	litres	water.

The two solutions are mixed as usual and the cotton is worked in the bath for about twenty minutes, squeezed, dried rapidly in a current of air at about 40° C., and the colour is then developed at a low temperature, 26 to 27° C., in a closed chamber, in which the same atmosphere is constantly circulated. All loss of aniline and oxidant is thus avoided and the fibre is not tendered. Six per cent. of aniline is sufficient to produce a full black. The bath differs from those usually employed in its heavy content in chloride of ammonium and acetate of copper.

VANADATE OF LEAD.

G. Friedlander (*R.G.M.C.*, p. 44, 1909) notes that the extraordinary efficacy of a proportion of a vanadium salt almost microscopic as compared with the total mass of the printing colour practically neutralises the expensiveness of vanadium compounds. This activity, however, necessitates great care in the preparation and use of the bath or printing colour made with these compounds. If the mixture is not perfectly uniform unlevel results on steaming are sure to follow. Moreover, the use of soluble vanadate entails precisely the same risks as the employment of other soluble metallic salts, that is premature formation of the black. These considerations naturally suggested that a body should be sought for combining the valuable properties of vanadium with insolubility in the bath or printing colour. This has been found in metavanadate of lead. A colour made with this will keep indefinitely, but when the fabric is steamed the vanadium goes into solution and acts in the usual manner. The salt is prepared as a white precipitate by mixing a solution of vanadium chloride with one of lead acetate. The metavanadate thus formed in suspension in water is used in the proportion that has hitherto been employed in the case of the soluble salts of vanadium. The presence of lead in the compound increases the fastness of blacks printed with it, and it may be used with either Diphenyl Black or Paramine Brown, also increasing the fastness of the dyeings or prints. The following is an exact recipe for the metavanadate of lead:—

10	grammes	ammonium vanadate,
70	„	distilled water,
5	„	glycerine,
50	„	hydrochloric acid 19° B.

Boil together until the solution turns blue. Then dilute with distilled water to 10,000 grammes and add the same volume of a one-tenth solution of acetate of lead until the liquid above the precipitate is colourless. The whole is ready for use when stirred up. The object of the hydrochloric acid in the recipe is to convert the ammonium vanadate into vanadium chloride as the original vanadium salt will not react with the lead acetate in the desired manner.

CHAPTER XII.—Paramine Brown.

In the preceding pages the attempts to transform bases other than aniline into colouring matters on the fibre have been recorded. A recent article on the subject by E. Grandmougin (*Z.F.*, 1906, p. 141) notes that one alone of all the numerous bases studied, paraphenylenediamine, seems to have had a lasting success. Its use was recommended by H. Schmid, and patented by the Badische Anilin und Soda Fabrik (*E.P.*, 17,247, 1905, *A.P.*, 863,761). The patented process furnishes a brown of perfect purity, and the paraphenylenediamine employed has been given the name of Paramine. With a chlorate as an oxidant it gives a fine brown, fast to air, light and soaping and fairly fast to chlorine. It may be used as a self colour, or with a white or colour resist, just in the same manner as aniline black, and is also used in direct printing.

Padding Process for Self Brown, or for White and Colour Discharges.

Run the bleached cotton material through the following liquor in padding machine:

15 to 20 grammes	Paramine, dissolved in
300 c.c.	hot water, dilute with
450 „	cold water, then add
1.5 gramme	Rongalite C., and when this is dissolved,
15 to 20 grammes	chlorate of soda, dissolved in
50 c.c.	water, and
15 to 20 grammes	sal ammoniac, dissolved in
50 c.c.	water, stir constantly, and add finally
15 „	vanadate of ammonia solution 1.1000,
30 to 40 „	tartar emetic, dissolved in glycerine.

Bring up to one litre. After standing for about an hour the solution becomes almost colourless; before use it must always be strained through a fine cotton cloth. The solution will keep at least two days. The Rongalite is added to reduce the oxidation product which commercial diamine frequently contains. For self browns after drying in the hot air chamber at 40 to 45° C., steam for five minutes in the Mather and Platt, then rinse and soap.

For white or colour discharges after drying in the hot air chamber print on one of the discharge pastes given below, dry and

steam for three to five minutes in the Mather and Platt as free from air as possible. For colour discharges hang up the goods for twenty-four hours to develop the colour effects, then pass through tartar emetic to complete the fixation of the colours, wash and soap lightly. Instead of hanging up the goods they may be given a passage through a lukewarm solution of bichromate of potash, 2 to 3 grammes per litre. A subsequent treatment with chlorine in the case of the white discharge is not to be recommended.

White Discharges.

1. 250 to 300 grammes Rongalite C,
750 to 700 „ gum thickening 1:1

2. 200 grammes gum thickening 1:1,
100 „ acetate of soda crystals,
200 „ sulphide of potash, 45 B,

- 375 to 350 grammes gum thickening 1:1,
125 to 150 „ Rongalite C.

Mix the two pastes.

Colour Discharges.

- 30 to 40 grammes dyestuff dissolved in
40 „ acetine, and
130 c.c. hot water,
220 grammes gum thickening 1:1.

Cool down to about 40 to 50° C., and add 230 grammes Rongalite C. When this is dissolved stir until cold, and add:

- 90 grammes aniline oil,
240 c.c. tannic acid in alcohol 3:4,

and stir up occasionally. To lessen the colouring power of this discharge paste, mix with it a thickening consisting of:

- 800 grammes gum thickening 1:1,
200 „ Rongalite C.

The following dyestuffs are suitable:—

Blue: Methylene Blue, NN and BG; Nile Blue, A.

Yellow: Auramine, O and G.; Euchrysine, GG, RD, and RRD; Thioflavine and Acridine Yellow.

Green: A blue and a yellow.

Pink: Rhodamine B extra, and 6G extra.

Red: Rhodamine B extra, and 6G extra, and Auramine O.

Orange: Acridine Orange.

The addition of tartar emetic solution to the padding liquor is for the purpose of retarding the oxidation of the Paramine. If padded in this way a pure white discharge can be obtained, even after the goods have lain for 12 to 18 hours; cloth padded without the tartar emetic solution in glycerine added to the paste soon becomes strongly tinged when exposed to the air, especially in the light, and a pure white is then no longer obtainable.

Tartar Emetic Solution.

40	grammes tartar emetic, dissolved in
620	„ warm water, add
340	„ glycerine.

Goods printed with the discharge colour, whether steamed or not, and also the self-brown, can be left to lie for some time without being injuriously affected.

Drying in the hot-air chamber is best carried out at a temperature of 40 to 50° C. The padded colours containing ammonium nitrate are somewhat better dischargeable than those produced with sal ammoniac. The brown can also be resisted with albumen colour lakes to which sulphite or acetate of soda has been added.

Direct Printing Process.

The goods prepared for printing as usual are printed with the following paste:

20 to 25	grammes Paramine, in
187	c.c hot water, add
635	grammes neutral starch tragacanth thickening,
3	„ Rongalite C., and
20 to 25	„ chlorate of soda, dissolved in
50	c.c. water, and
20 to 25	grammes sal ammoniac, or
25 to 30	„ ammonium nitrate in
50	c.c. water.

Immediately before printing add 20 c.c. of vanadate of ammonia solution, 1: 1000 per litre of colour. After printing, dry, steam for 4 to 5 minutes in the Mather and Platt, rinse, and soap.

This printing paste will keep only for a limited time.

Instead of passing the goods through the Mather and Platt, they may be steamed for a longer time in the continuous steamer, or in the cottage steamer. This allows Paramine Brown to be used together with basic and alizarine dyestuffs, or with steam colours on beta-naphthol prepared cloth.

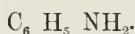
J. Langer (*Z.F.*, 1906, p. 344) gives a detailed and very interesting description of effects on flannelette, obtained with white or colour discharges over Paramine. Langer, among other things, mentions that discharge pastes containing sulphite of potash and

acetate of soda, together with the Rongalite or Hydrosulphite NF, give still better results than those obtained with the hydrosulphites alone.

Since the introduction of Paramine Brown an extra brand has been put on the market under the name of Paramine extra. Paramine Brown has found much favour in calico printing, for the production of fast browns for resist and discharge styles. This has led to a demand for a brown with similar properties, but with a yellower tone, and Fuscamine G has recently been put upon the market to fulfil this requirement. The method of application is similar to that employed for steam aniline black. Fuscamine G is suitable either for direct printing or for padded shades, which can be discharged to a pure white with Rongalite C.

CHAPTER XIII.—Examination of the Principal Dyewares used in Dyeing and Printing Aniline Black.

ANILINE.



Chemically pure aniline is a colourless, oily liquid, the specific gravity, at 15° C., is 1.0265; it boils at 182° C., is soluble in 32 parts of water at 15° C., and is volatile on steaming.

Commercial aniline, ordinarily used in dyeing and printing, is the "aniline for blue," obtained from the finest benzols. It usually contains a little water, a slight amount of ortho- and para-toluidine, and sometimes traces of ammonia, nitro-benzene, nitrotoluene and sulphur compounds (aminothiophene?). The total impurity, not including the water, should be well under half per cent. Good commercial anilines may be considered as chemically pure, and give a perfectly limpid solution in hydrochloric acid.

The following are the most important tests used by dyers and colourists to ascertain if a commercial aniline fulfills the above conditions:—

Distillation test.—Distil 200 grammes of the sample in a fractionating flask. The temperature must be indicated by a very exact thermometer with the mercury bulb a little below the place where the lateral tube is in communication with the neck of the flask. The aniline passed over between 181 and 182° C. is collected in a tared flask. It should be at least 192 grammes, 96 per cent. of the sample tested.

The boiling point varies with the barometric pressure, the oil which passes over within the space of 1° C. is considered to be perfectly pure. The content in water may also, of course, be noted, during distillation. The presence of water can also be proved by shaking up the aniline, if it froths, water is present. To dry aniline dry caustic soda or potash must be used, not chloride of calcium.

Printing test.—Dissolve 16 grammes of the aniline in 12½ grammes of hydrochloric acid, 21° B., diluted with 20 grammes of water, add 300 grammes of thickening and immediately before printing add 3 grammes of sulphide of copper paste.

Prepare the thickening by boiling 75 grammes of starch in 525 grammes of water and add 16 grammes of chlorate of soda dissolved in 70 grammes of water.

After printing, hang up the material for 36 hours in the moist chamber, at about 30° C., or pass it through the Mather and Platt along with a batch of goods.

Then chrome in $\frac{1}{2}$ gramme of bichromate of potash dissolved in 5 litres of water at 80° C. and $1\frac{1}{2}$ gramme of sulphuric acid, 66° B.

Wash lukewarm with 4 grammes of soap per litre, rinse and dry.

Dyeing test.—This is done in the same way as the printing test, using 10 grammes of starch in place of 75. Leas of wetted out, unbleached yarn, each 20 grammes in weight, are impregnated in this bath, wrung out, soaked again in the bath, wrung out again, then developed by ageing, and chromed and soaped in the usual way.

Kertesz recommends the following method:—For 50 grammes of cotton yarn dissolve $3\frac{1}{2}$ grammes of the aniline to be tested in 10 grammes of hydrochloric acid and 10 grammes of water. Prepare separately a solution of $5\frac{1}{2}$ grammes of bichromate of potash in 500 grammes of cold water. Mix the two solutions, work the yarn for half an hour in the cold bath, heat it up slowly to 60° C., and finish the dyeing at this temperature. Wash thoroughly and soap lukewarm.

It must be noted here that the tests by dyeing and printing do not gauge accurately the richness of the sample in pure aniline. The only conclusive test of this is by distillation. From the practical point of view, however, the best test is that made under the same conditions as in working on a large scale.

As we have already said, many dyers in place of pure aniline use mixtures of this alkaloid with toluidine and other homologues. These mixtures are known as “aniline for red.” As a rough test these special oils can be valued by comparing their specific gravities and boiling points with a known oil that gives satisfactory results. It is not necessary to say that it is better to complete the test by a comparison of prints or dyeings.

ANILINE SALT.



Pure aniline salt or hydrochloride of aniline crystallises in needles or in large leaf-like crystals; it dissolves easily in water or alcohol and melts at 92° C.

Commercial aniline salt is on the market in this form or in colourless or greyish plates, or it is melted and sent out in irregular lumps. It is tested to determine its content in water, in pure hydrochloride, in hydrochloric acid or in free aniline, in common salt, or in sal ammoniac.

Moisture.—Weigh about 4 grammes in a flat glass tube, dry over sulphuric acid, leave the salt in the dessicator until the weight is constant.

Free acid.—Aniline salt is prepared on a large scale by mixing 100 parts of aniline and 130 to 135 parts hydrochloric acid in an earthenware vessel. It is left to cool and until no more crystals are deposited. The mother-liquor is then decanted, the crystals

are centrifuged and then dried thoroughly by heat. This method of preparation frequently leaves in the salt a certain quantity of free acid.

The test is made with magenta paper, simply prepared by steeping filter paper in a solution of magenta, 1 gramme per litre. Free acid strips the colour from this paper. Methyl violet paper turns green.

To make a quantitative test arrange in a row three small flasks, each to contain about 200 c.c. In the first two dissolve 5 grammes of the salt to be examined in 100 c.c. of water, and in the third put 100 c.c. of distilled water. To each of the three add 1 c.c. of a solution of crystal violet, 1 gramme per litre of water, then titrate the solution in the first flask with decinormal soda until the solution, which has turned blue under the action of the hydrochloric acid, takes the colour of the neutral solution of crystal violet. The No. 2 and No. 3 flasks serve as points of comparison. With a little practice the final point of the reaction is exactly determined. The percentage of free acid is then easily calculated. For instance, 5 grammes of the salt have required for neutralisation 10.7 c.c. of decinormal soda. As 1 c.c. of decinormal soda represent 0.00365 HCl, the 5 grammes of aniline salt contain $.000365 \times 10.7 = 0.0039055$ HCl, or 0.78 per cent.

The total hydrochloric acid can be quantified by means of normal soda with phenol-phtalein as indicator.

Content in pure hydrochloride of aniline.—This is ascertained by determining the quantity of aniline obtained by decomposing a given quantity of the salt with caustic soda.

Pour a solution of 20 grammes of the salt in 40 c.c. of hot water into a graduated 200 c.c. flask with an emery stopper. Add 7 grammes of caustic soda dissolved in 20 c.c. of water, or 20 grammes of caustic soda lye at 30° B., and 30 grammes of common salt. Shake up several times, allow to cool and bring up to 200 c.c. with distilled water. When the temperature has fallen to 15° C. read off the number of c.c. occupied by the aniline which has separated out. This number multiplied by 5.130, that is, the specific gravity of aniline multiplied by 5, gives the percentage by weight of the salt in aniline; 71.8 of aniline represent 100 of hydrochloride; according to the quantity of aniline the proportion of pure salt in the hydrochloride can easily be deduced.

The following process can also be recommended:—Decompose 300 grammes of the aniline salt by means of caustic soda in a large graduated burette. Measure the aniline set at liberty, then syphon off the aqueous liquid. Dry for a night with some pieces of caustic soda or caustic potash and distil as above.

Mineral impurities and adulterations.—Treat a known weight of the aniline salt with absolute alcohol until this dissolves no more of the salt. If there is a residue it consists of impurities or adulterants, the nature of which can be easily ascertained by the

ordinary methods of analysis. Aniline salt sometimes contains common salt.

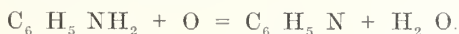
CHLORATE OF POTASH.



Chlorate of potash is sent out in small brilliant crystals, anhydrous and stable in the air, or in a crystalline powder. The solution should have neither an acid nor an alkaline reaction. The salt dissolves in 16 parts of cold water and in 3 parts of hot water.

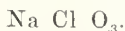
Prepare a solution of 3 grammes of the chlorate in 60 c.c. of water. Add 10 c.c. of water saturated with sulphuretted hydrogen to 10 c.c. of this solution. The mixture should neither be turbid nor coloured, which would indicate the presence of lead. Test another 10 c.c. of the solution with oxalate of ammonia for salts of calcium and with nitrate of silver for chlorides of calcium or potassium. Adulteration with nitrates, saltpetre in particular, which is sometimes met with, is recognised by the ammoniacal odour when 1 gramme of the salt is heated in a test tube with 5 c.c. of soda lye, $\frac{1}{2}$ gramme of granulated zinc, and $\frac{1}{2}$ gramme of iron filings, which can be replaced by 1 gramme of aluminium dust.

Theoretically, the formation of aniline black requires 31.7 of the weight of the aniline salt of chlorate of potash if the following equation is accepted as correct:—



The simplest formula for the base of aniline black is $\text{C}_6 \text{ H}_5 \text{ N}$, but as we have seen, the latest researches of Willstaetter have led him to adopt the formula $\text{C}_{12} \text{ H}_9 \text{ N}_2$. Assuming that this is correct, the theoretical quantity of chlorate of potash required is 47.55. In practice less than 40 per cent. of chlorate is rarely employed. The content of chloric acid may be determined by means of E. Felli's apparatus (*B.S.M.*, 1900, p. 153), but the test is rarely necessary, as chlorate of potash is usually sent out in a very satisfactorily pure state.

CHLORATE OF SODA.

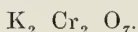


This is sent out in colourless crystals. It is soluble in its own weight of cold water whereas, as we have noted, chlorate of potash requires 16 times its own weight of cold water. As 87 parts of chlorate of soda replace 100 parts of chlorate of potash and the latter has the fault of crystallising out of the printing pastes, chlorate of soda is almost always preferred.

Chlorate of soda is tested in the same way as chlorate of potash, but as it is hygroscopic it should be tested for moisture. It sometimes contains chloride of sodium when it has been prepared by electrolysis. The chloric acid is titrated by means of Mohr's salt,

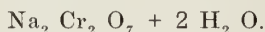
ammoniacal ferrous sulphate. A 5 to 10 per cent. solution of chlorate is treated with an excess of semi-normal Mohr's salt and a large excess of sulphuric acid 1: 3, allowed to rest for ten minutes, and the excess of ferrous salt is quantified with a deci-normal solution of permanganate of potassium.

BICHROMATE OF POTASH.



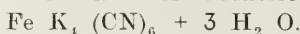
This salt is sent out in a very pure state in the form of triclinic prisms of an orange red colour. It is anhydrous, stable in the air, and dissolves in about ten times its weight of cold water. It is generally unnecessary to test as commercial bichromate of potash is almost chemically pure.

BICHROMATE OF SODA.



Bichromate of soda also crystallises in red prisms. It is much more soluble than bichromate of potash. 101.6 parts of pure bichromate of soda are required to replace 100 of bichromate of potash. It can be tested by titrating with ammoniacal sulphate of iron or by quantifying the iodine set at liberty in an acidulated solution of iodide of potassium.

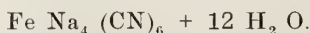
FERROCYANIDE OF POTASSIUM.



"Yellow prussiate" crystallises in lemon yellow octagons. It has a bitter-sweet saline taste. It dissolves in 4 parts of cold water and in 2 parts of boiling water. It usually contains sulphate of potash and sometimes ferrocyanide of sodium, which is a less expensive salt. It is, of course, easy to detect this adulteration by analysis.

Titrate with permanganate of potash:—Dissolve 0.9 gramme of the salt to be tested in 100 c.c. of water in a porcelain capsule. Drop in the permanganate until there is a persistent pink colouration. It is not easy to recognise the exact point at which the reaction terminates. When sulphuric acid is added the prussiate solution becomes milky and turns slightly blue; on the addition of permanganate it becomes yellow, then green; successive additions bring it gradually to the final pink colouration. Haën has recognised the difficulty of precisely determining the final point of the operation. He recommends the titration with permanganate should be regulated with pure ferrocyanide of potassium instead of following the usual laboratory practice of preparing the standard solution with iron wire.

FERROCYANIDE OF SODIUM.



This strongly resembles the potassium salt. It is also in yellow crystals, which effloresce in the air and dissolve in $4\frac{1}{2}$ parts of cold water. It is tested in the same manner as the potassium salt.

CHAPTER XIV.—Testing Aniline Black Dyeings.

Aniline black dyeings may have to be examined from several points of view. The following questions may arise, for instance: Does the colour rub? To what extent has the fibre been tendered by the processes through which it has passed? Does the black turn green under the action of sulphurous acid?

It might be supposed that the extent of the change of shade of the black under the influence of sulphurous acid is an indication of a corresponding fastness of the dyeing to air and light; as a matter of fact, these two qualities of fastness have nothing in common. For instance, the black obtained by Monnet's process with aniline and paraphenylenediamine after three months' exposure to the air, from July to September, was much more changed than that obtained with aniline; whereas this latter black turned green under the influence of sulphurous acid, while Monnet's black simply took a brownish tone.

The test with sulphurous acid cannot, therefore, replace that made by exposure to the air and light, and this must be undertaken independently.

To test with sulphurous acid prepare the following bath:—

20	c.c.	bisulphite of soda,	28	B.,
20	„	hydrochloric acid,	21	B.,
580	„	cold water.		

Steep the dyeing to be examined in this mixture, let it remain ten minutes, rinse thoroughly in distilled water, and dry.

The following test is more conclusive:

Pour 50 c.c. of bisulphite of potash and 50 c.c. of hydrochloric acid into a litre flask, moisten the dyeing to be tested, and hang it over the open neck of the flask, leaving it to the action of the gaseous sulphurous acid for several hours, then wash and dry. A black which resists this treatment without changing may be considered to be completely ungreenable.

F. Dannerth, in his recently-published work, "The Methods of Textile Chemistry," suggests the following as the necessary tests:

1. Determine the tensile strength of the fabric before and after dyeing.
2. Determine the amount of mineral matter in the finished fabric.

In goods which have been imperfectly washed chromium will be found. Logwood blacks leave an ash containing iron, and can therefore be readily distinguished.

3. Determine the fastness of the finished black to soap, soda, light, greening, acids, perspiration, and crocking.

4. Examine the black for its quality. The various blacks found on cotton goods dyed by different methods have blue, red, or green casts. The intensity of the black depends among other things on the amount of aniline oil used.

5. Tests for blacks encountered on cotton goods, as compared with aniline black:

Bleaching powder: A 35° B. solution intensifies aniline black. A 3° B. solution turns aniline black a red brown.

Stannous chloride (with hydrochloric acid)—colour not affected. Distinction from sulphur black.

Sodium hydrosulphite—colour removed but returns on washing. Distinction from diazo blacks.

Boiling water—colour unaffected and water remains clear. Distinction from direct blacks.

Boiling dilute sulphuric acid—colour does not turn red. Distinction from logwood black.

In view of the fact that black is often obtained by mixtures the above tests are not sufficient. A thorough analysis is a difficult process.

G. Capron (*R.G.M.C.*, 1907, pp. 129 and 236) has published a series of tables of tests for a large number of blacks. He also gives a methodical system of analysis allowing the nature of the colouring matter to be determined.

A. G. Green has also published analytical tables with the same object, and we understand these will shortly be issued in book form. These tables are the most complete, and at the same time the least complicated, as yet at the service of the chemist.

CHAPTER XV.—Recipes and Processes for the Patterns.

Nos. 1 and 2 Sulphide of Copper Blacks. These patterns, showing two different finishes, have been supplied by Read Holliday and Sons, Ltd., of Huddersfield, whose aniline oil was used in the dyebath.

Nos. 3 and 4 Prussiate Blacks. Messrs. Read Holliday's aniline oil, was also used for these two patterns, one of which shows a coloured selvedge.

No. 5. Bobœuf's Black. See page 150.

The six following patterns show basic colour resists.

No. 6 Yellow Resist under Aniline Black.

Aniline Black Liquor.

- | | |
|----|--|
| A. | 33.6 grammes chlorate of soda dissolved in |
| | 273 „ water. |
| B. | 42 grammes ferrocyanide of potash dissolved in |
| | 273 „ water. |
| C. | 54 grammes aniline oil in |
| | 52.6 „ hydrochloric acid 22° B. |
| | 271.8 „ water. |

Mix A., B., and C. together cold.

Pad on, dry at about 50° C., and print as quickly as possible with

Yellow Resist.

- | | |
|------------|--|
| 10 grammes | Rhoduline Yellow T (By), |
| 120 „ | water, |
| 70 „ | acetic acid 6° B., when dissolved, stir in |
| 800 „ | Resist W. |

Resist W.

- | | |
|-------------|-------------------------------------|
| 387 grammes | water, |
| 129 „ | acetate of soda, |
| 65 „ | oxide of zinc, mix well and stir in |
| 258 „ | British gum. |

Boil and add when cold:—

- | | |
|-------------|----------|
| 161 grammes | albumen. |
|-------------|----------|

Run the printed pieces for four minutes through the Mather and Platt, then full width through silicate of soda at 40° C., rinse and dry.

No. 7, Green Resist under Aniline Black.

7 grammes Rhoduline Yellow T (By),

4 „ Turquoise Blue G (By).

Otherwise as in No. 6.

No. 8, Violet Resist under Aniline Black.

8 grammes Crystal Violet P (By).

Otherwise as in No. 6.

No. 9, Yellow Resist (red shade) under Aniline Black.

15 grammes Coriphosphine OX extra (By).

Otherwise as in No. 6.

No. 10, Heliotrope Resist under Aniline Black.

15 grammes Rhoduline Heliotrope BB (By).

Otherwise as in No. 6.

No. 11, Red Resist under Aniline Black.

15 grammes Rhoduline Red G (By).

Otherwise as in No. 6.

The four following patterns show resists obtained with the Benzo Colours.

The aniline black liquor and the treatment of the goods as in No. 6.

No. 12, RED RESIST UNDER ANILINE BLACK.

20 grammes Brilliant Congo R (By),

80 „ water, when dissolved add

800 „ Resist B,

100 „ albumen 1:1.

Resist B.

200 grammes oxide of zinc, in

95 „ water, add

40 „ turpentine,

20 „ glycerine,

10 „ chalk,

10 „ caustic soda 36° B.,

600 „ British gum 1:1,

25 „ water.

Crimp Effect.

After development, print on a stripe with gum water 1:1, dry, run through caustic soda 30° B., rinse well, acidulate with acetic acid, rinse again and dry.

No. 13, Blue Resist under Aniline Black.

20 grammes Brilliant Benzo Blue 6B (By).

Otherwise as in No. 12.

No. 14, Yellow Resist under Aniline Black.

20 grammes Thiazole Yellow 3G (By).

Otherwise as in No. 12.

No. 15, Green Resist under Aniline Black.

10 grammes Brilliant Benzo Blue 6B (By),

15 „ Thiazole Yellow 3G (By).

Otherwise as in No. 12.

No. 16, Heliotrope Resist under Aniline Black.

As in No. 10, but with crimp effect as in No. 12.

No. 17, Red Resist under Aniline Black.

As in No. 11, but with crimp effect as in No. 12.

No. 18, Diazo Black BHN.

For 100 kilos. cotton material with worsted selvedges, prepare the dye bath with—

1 kilo Diazo Black BHN (By),

10 „ Glauber's salt crystals,

$\frac{1}{2}$ „ soda ash

Dye at 40° C.

No. 19, Diazo Black BHN, topped with Aniline Black.

The cotton material with worsted selvedges is dyed as above, and then topped with aniline black.

The aniline black has been padded on. The material has the Schreiner finish.

No. 20, Paramine Extra on Flannelette.

For method of working, see Chapter XII. The use of Paramine extra according to this recipe is patented by the Badische Anilin und Soda Fabrik, but purchasers of Paramine extra are granted licenses entitling them to work the process.

No. 21, Diphenyl Black Base I. print on bleached goods in Combination with Alizarines.

Diphenyl Black Base I.

600 grammes acid starch thickening,

20 „ olive oil,

30 „ sodium chlorate, in

50 „ water,

35 „ Diphenyl Black Base I. (M.L. & B.) in

100 „ acetic acid, 6° B., and

30 „ lactic acid, 50 %

18 „ aluminium chloride 30° B.,

15 „ copper sulphide paste 30 % and

2 „ ammonium vanadate, 1:1,000 in

100 „ water.

Alizarine Red Printing Colour.

550	grammes	thickening for red, well mixed with
40	„	Lizarol D. Conc. (M. L. & B.),
120	„	Alizarine D 4NG paste 20 %,
105	„	aluminium sulpho-cyanide 12° B,
35	„	aluminium acetate 11° B,
10	„	tin oxalate 16° B,
40	„	calcium acetate 18° B,
3	„	tartaric acid,
97	„	water.

Green KR.

10	grammes	Alizarine Yellow KR (M. L. & B.),
314	„	water,
550	„	acid starch thickening,
1.8	„	Methylene Blue D BB (M. L. & B.),
50	„	water,
25	„	acetic acid 6° B,
50	„	chromium acetate 20° B.

Alizarine Pink Printing Colour.

400	grammes	acid starch thickening, with
200	„	gum tragacanth (60 : 1,000), and
15	„	Lizarol D conc.,
20	„	glycerine,
10	„	Alizarine D I B paste 20 %,
45	„	water,
30	„	aluminium sulphocyanide 12° B,
5	„	calcium acetate 18° B,
275	„	water.

Thickening for Red.

1,000	grammes	wheat starch,
200	„	wheat flour,
7,500	„	water,
350	„	tragacanth (60 : 1,000),
650	„	acetic acid 6° B.

Boil ten minutes, and add:

300 grammes olive oil.

Acid Starch Thickening.

2,100	grammes	wheat starch,
5,700	„	water,
2,200	„	acetic acid 6° B.

Steam after printing for one minute in the Mather and Platt, and one hour in the continuous steamer.

No. 22, Diphenyl Black Print in Combination with Alizarine Blue.

Diphenyl Black Oil DO.

110	grammes	wheat starch in
531.5	„	water, and
112.5	„	acetic acid 6° B.,
20	„	olive oil.

Boil half an hour, and add, while still warm,
25 grammes sodium chlorate.

When cold, add :

50	grammes	Diphenyl Black oil DO (M. L. & B.),
22.5	„	lactic acid 50 %,
12.3	„	1 hydrochloric acid 18° B,
6.7	„	water.

Immediately before using, add :

20	grammes	copper sulphide paste 30 %, in
63	„	water,
21.5	„	aluminium chloride 30° B.

Steam one minute in the Mather and Platt, and one hour in the continuous steamer. Pass at 60° C through a bath containing 3 grammes of soda and 2 grammes of soap per litre and rinse.

No. 23 Diphenyl Black for Covers.

26	grammes	Diphenyl Black Base I. (M. L. & B.) in
100	„	acetic acid 60° B,
17	„	aniline oil, and
16.8	„	hydrochloric acid 17.5° B.,
650	„	acid starch thickening,
23	„	sodium chlorate, in
60	„	water,
2	„	copper chloride 40° B,
16	„	aluminium chloride 17.7° B, and
22	„	copper sulphide paste 30 %, in
67.2	„	water.

Steam two minutes in the Mather and Platt, pass at 60° C. through a bath containing 3 grammes of soda and 2 of soap per litre, and rinse.

No. 24, White Resist under Diphenyl Black.

Ground Print.

Diphenyl Black oil DO and white resist.

Cover Print.

Diphenyl Black Printing Colour, as in No. 21.

White Resist.

110	grammes	water,
22	„	soda ash,
110	„	sodium bisulphite.

Boil till all evolution of carbon dioxide ceases, and add :

310	grammes	British gum in
150	„	water, and
132	„	gum solution 1: 1,
66	„	sodium acetate,
110	„	thiosulphate.

Steam after covering for two minutes in the Mather and Platt. Pass at 60° C. through a bath containing 3 grammes of carbonate of soda, and 2 grammes of soap per litre, and rinse.

No. 25, Diphenyl Black on Naphthol Prepare in Combination with Para Red.

Prepare.

25	grammes	beta naphthol R,
25	„	caustic soda 40° B,
20	„	Para soap PN (M. L. and B.),
3	„	tartar emetic,
5	„	glycerine,

Per 1 litre water.

Black Printing Colour.

500	grammes	gum tragacanth (60: 1,000),
100	„	China clay paste 1: 1, and
57	„	aniline salt,
16	„	Diphenyl Black Base I,
5	„	paraphenylenediamine,
12	„	aniline oil. and
50	„	acetic acid 6° B.,
20	„	aluminium chloride 30° B.,
30	„	sodium chlorate in
71	„	water,
20	„	copper sulphide paste 30 %, in
105	„	water,
15	„	ammonium vanadate 1: 1,000.

Red Printing Colour.

22	grammes	paranitraniline, well pasted with
42	c.c.	nitrite solution 290/1,000, and
80	„	cold water.

Stir slowly into a mixture of

250 grammes ice and water.

Then add

35.2 c.c. hydrochloric acid 22° B.

After standing 15 minutes, filter and make up to 500 c.c., and stir into

500 grammes tragacanth 60: 1,000.

Immediately before use add 40 grammes of sodium acetate crystals.

Prepare in naphthol, dry, print on the two colours, steam one minute in the Mather and Platt, pass at 60° C. through a bath containing 3 grammes of soda and 2 grammes of soap per litre, and rinse.

No. 26, Diphenyl Black Print on a Naphthol Prepare, and then Dyed with Paranitraniline.

Naphthol Prepare.

16	grammes	beta naphthol.
16	„	caustic soda 40° B,
15	„	Para soap PN,
3	„	tartar emetic,
5	„	glycerine.

Per 1 litre water.

Black Printing Colour.

As in Pattern No. 25.

Developing Bath.

14	grammes	paranitraniline extra	pasted with
10	c.c.	water.	

Cool and mix with

26	c.c.	nitrite solution	290/1,000,
and stir into a mixture of			
22	c.c.	hydrochloric acid	22° B, and
200	„	ice water and ice.	

After a thorough stirring, filter. Immediately before use mix with 30 grammes sodium acetate crystals and make up to one litre.

The process is as in pattern No. 25. Prepare the goods with a naphthol prepare, dry, print with Diphenyl Black, steam one minute in the Mather and Platt, pass at 60° C., through a bath containing 3 grammes of carbonate of soda, and 2 grammes of soap per litre, and rinse.

No. 27, Diphenyl Black Print on Cotton Yarn.

No. 28, Diphenyl Black in Combination with Indigo M. L. B. /4 B.

Diphenyl Black Printing Colour.

50	grammes	Diphenyl Black oil	DO in paste, per 1,000
		grammes.	

Recipe as for No. 22.

Indigo Printing Colour.

12	grammes	Indigo M. L. B./4 B	paste,
40	„	glycerine.	
50	„	caustic soda 40° B.	
6	„	Hydrosulphite NF conc.	1 : 1,
325	„	British gum	1 : 1.

When the indigo is reduced on heating add

325	grammes	British gum	1 : 1,
60	„	potassium sulphite	45° B.,
50	„	olive oil,	
132	„	water,	
8	„	Hydrosulphite NF conc.	1 : 1.

Print the two colours, dry, steam three minutes in the Mather and Platt, pass at 60° C. through a bath containing 3 grammes of soda and 2 grammes of soap per litre, and rinse.

No. 29 Diphenyl Black Oil DO on Velveteen.

Padding Bath.

50 grammes	Diphenyl Black oil DO in
50 c.c.	acetic acid 8° B., 50 %,
40 „	lactic acid 50 %, and
12 „	hydrochloric acid 19° B.
100 grammes	gum tragacanth (60 : 1,000) in
300 „	water.
25 „	sodium chlorate in
50 „	water.
17 c.c.	aluminium chloride 30° B.,
2 „	copper chloride 40° B.,
400 „	water.

Steam two minutes in the Mather and Platt, rinse and soap.

No. 30 Diphenyl Black Base I on Half Silk.

Padding Bath

60 grammes	tragacanth 1 : 10, diluted with
75 „	water,
40 „	Diphenyl Black Base I dissolved in
50 „	lactic acid and
130 „	acetic acid 40 %.

Stir into the tragacanth together with

145 grammes water.

Make up to 5 kilos.

25 grammes	aluminium chloride 30° B.,
25 „	chromium chloride 30° B.,
4 „	copper chloride 40° B.,
346 „	water,
30 „	sodium chlorate dissolved in
60 „	hot water. Then add
10 „	turpentine.

Make up to 5 kilos.

Mix the two solutions immediately before use. Steam three minutes in the Mather and Platt, rinse and soap.

No. 31, Yellow Resist under Aniline Black.

Yellow Resist.

40 grammes	Thioflavine T (Cassella),
110 „	water,
150 „	acetic acid, 5° B.

When dissolved mix in

200 grammes acid starch tragacanth thickening,
and when cold add

500 grammes White Resist Z.

White Resist Z.

350	grammes	acid starch tragacanth thickening
250	„	zinc white,
350	„	acetate of soda,
50	„	tin crystals.

Print on, dry, steam for a short time in the Mather and Platt, chrome lukewarm with 5 grammes of bichromate of potash and 2 grammes of soda per litre, wash and dry.

Padding Bath.

289	grammes	hydrochloride of aniline,
186	„	ferrocyanide of potash,
93	„	chlorate of soda.

Bring up each separately to 1,000 grammes with water, mix the three solutions cold in equal portions, pad over the printed cloth and dry in the hot flue.

No. 32, Black Print Acting as Resist under Aniline Black.

Printing Paste.

4	grammes	Immedial Carbon B for Printing (Cassella).
3	„	Immedial Bordeaux G conc. (Cassella).

Stir thoroughly into a paste with

20 grammes glycerine,

and heat with

40	grammes	Hyraldite C extra 1 : 1,
20	„	caustic soda lye, 40° B.,
420	„	water.

for about a quarter of an hour at 60° C., when cold stir in

500 grammes alkaline thickening.

Alkaline Thickening.

50	grammes	wheat starch,
250	„	water,
100	„	British gum,
600	„	caustic soda lye, 40° B.

Boil together and allow to cool.

Print on, dry, steam for two minutes in the Mather and Platt at 100° C. No black is developed at the parts printed with the Immedial Colours. Finally wash in warm water and dry.

No. 33, Red and White Pigments over Prussiate Black.

Red.

80	grammes	British gum,
270	„	warm water,
500	„	Express Red B. (Wegelin, Tetaz and Co.).

Heat together until completely dissolved at 70 to 80° C., and while still warm add

150 grammes oxide of zinc.

Cool down and sieve.

White.

200 grammes Snow White G. (Wegelin, Tetaz and Co.),
1 litre gum tragacanth 6 : 100.

Print on cloth prepared with prussiate aniline black, dry and steam for two to three minutes in the Mather and Platt, then chrome with 5 grammes per litre, wash well and soap, if necessary.

No. 34, Lactate of Aniline (Oxidation) Black.

Pad with a solution containing per litre:—

70	grammes	Aniline Salt (Chem. Fab. Griesheim-Elektron),
16.7	„	Aniline Oil (Chem. Fab. Griesheim-Elektron),
35	„	lactic acid 50 %
24	„	sodium chlorate,
4	„	sulphate of copper.

After-treat with 15 grammes of bichromate and 5 grammes of Aniline Salt per litre and finally with 2 grammes of soap and 1 gramme of soda per litre.

No. 35 Prussiate (Steam) Black.

80	grammes	Aniline Salt (Chem. Fab. Griesheim-Elektron),
15	„	Aniline Oil (Chem. Fab. Griesheim-Elektron),
30	„	sodium chlorate,
60	„	yellow prussiate.

Dissolve separately, mix cold and bring up to one litre.

White Discharge.

500	grammes	gum arabic 1 : 2,
150	„	bisulphite 37.5° B.,
350	„	caustic soda lye 37.5° B.,
0.5	„	Azorubine, dissolved in a little water.

Print on, steam for two to three minutes at 94 to 96° C. in the Mather and Platt, and treat with 5 grammes of soda ash and 5 grammes of bichrome per litre at 50° C.

No. 36, Aniline Black on Half Wool.

This is produced by Könitzer's patented process. See page 140. The black is after-chromed.

The patentee is prepared to grant licenses for the employment of his process in Great Britain.

Nos. 37 and 38, A. G. Green's Patent Black.

For the process see page 78. Each of these patterns has been dyed with 3 % aniline. The second pattern has a Shreiner finish.

No. 39, Ciba Blue 2 BD paste with Sulphide of Copper Black.

The Ciba Colours of the Society of Chemical Industry in Basle may be printed in conjunction with steam aniline black. The goods are treated by the ordinary process, as neither prolonged

steaming nor after treatment with bichrome has any harmful effect on the Ciba colours. Finally the goods are soaped as usual.

No. 40, Ciba Violet B Paste with Sulphide of Copper Black.

No. 41, Ciba Bordeaux B Paste with Sulphide of Copper Black.

No. 42, Ciba Heliotrope B Paste with Sulphide of Copper Black.

The Ciba Colours are vat dyes, but the printing pastes are only slightly alkaline. The dyestuff is reduced with hydrosulphite to the leuco derivative soluble in alkali. This is fixed as usual by ageing or steaming and developed by soaping at the boil.

Nos. 43 and 44 Carbalin Resist Colours under Aniline Black.

Carbalin Resist Colours are sent out by the Fabriques de Produits Chimiques de Thann et de Mulhouse. They are lakes that can be fixed without albumen. Carbalin itself is a specially prepared carbonate of lime. They give very bright colours and do not harden the cloth as in the case of albumen pigments. They do not clog the lines of the engraving and allow large designs to be printed under aniline black. The colours are very fast to washing, and the printed cloth may be stored away for any length of time before padding in the bath for black. They are specially suitable for resisting vanadium aniline black, Paramine Brown and all other oxidation colours developed with vanadium. Any mixture of the colours may be made and printed on white goods with or without Carbalin. Slop pad the bleached cloth in a three-bowl padding machine, applying strong pressure, with the following cold bath:—

- | | | |
|----|---------------|-------------------------------|
| A. | 1,200 grammes | chlorate of soda in |
| | 12,800 „ | water. |
| B. | 2,160 grammes | yellow prussiate of potash in |
| | 11,200 „ | water. |
| C. | 3,360 grammes | Aniline Salt in |
| | 8,800 „ | water, |
| | 1,500 „ | gum tragacanth 50 : 1,000. |

Mix A B and C immediately before use, as the mixed solution does not keep long. After padding dry carefully, preferably in hot air, and print without delay, as the black develops slowly, even at the ordinary temperature.

- | | |
|--------------------|-----------------------------|
| 500 to 400 grammes | Carbalin colour, |
| 225 „ 200 „ | albumen solution, 50 %, |
| 125 „ 75 „ | acetate of soda, |
| 150 „ 325 „ | gum tragacanth. 50 : 1,000. |

After printing run through the small steaming box of the Mather and Platt for two minutes at 100° C., then pass through a bath of bichromate of soda, 50 grammes per litre at 40 to 50° C., wash and dry.

No. 45, Carbalin and Carbalin Resist Colours under Aniline Black.

100 to 200	grammes	Carbalin Resist Colour,
50	„ 70	„ glycerine,
30	„ 50	„ ammonia risinate 40 %,
620	„ 480	„ gum thickening neutralised with ammonia,
200	„	Carbalin.

Print on bleached goods, steam for 15 to 20 minutes, then pad in the following:—

A. 530 grammes Aniline Salt,
2,000 „ water.

B. 432 grammes yellow prussiate of potash (this may be substituted by a 15 to 30 c.c. vanadium chloride solution of 1 %, which permits of a stronger concentration of the aniline black solution)
2,000 „ water.

C. 240 grammes chlorate of soda,
2,000 „ water.

Mix A B and C and thicken slightly with 500 grammes gum tragacanth 60 : 1,000.

Pad on a machine with three rollers, the lowest of which, covered with 4 to 6 m.m. felt, partly dips into the aniline black solution and wets the second lowest roller, also covered with 3 to 4 m.m. felt, so that the printed piece, passing through the two upper rollers is just sufficiently wetted on one side. The thickness of the felt and the pressure of the rollers should be so arranged that no excess of solution comes into contact with the piece. This may also be attained by means of a two roller padding machine by attaching a rail or roller to the lower roller cased in felt in order to remove any excess of solution before reaching the piece.

After padding dry, develop the black in the usual manner and finish.

A plastic white may be obtained with prussiate aniline black by the addition of about 3 % of oxide of zinc to the Carbalin reserve print colour. After the bichromate and chalk or bichrome and Carbalin bath the colours should be brightened with a 3 % bath of acetic acid. The Carbalin colours are as follow:—Carbalin, Carbalin Pink AB, Carbalin Cutch A, Carbalin Yellow AL, Carbalin Blue F, Carbalin Violet U, Carbalin Orange D, Carbalin Green AL, Carbalin Red BP, and Carbalin Grey N.

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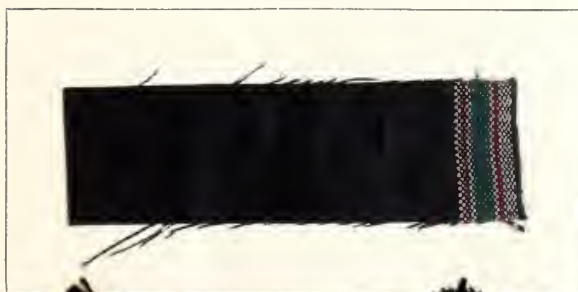
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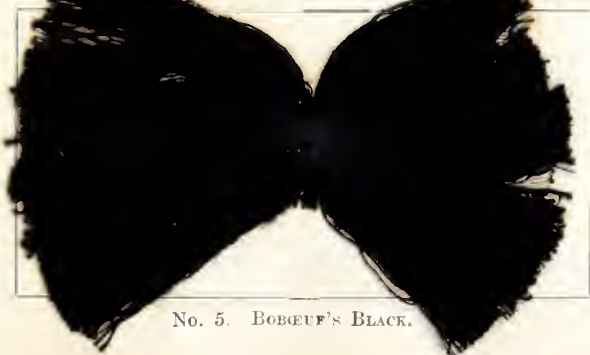
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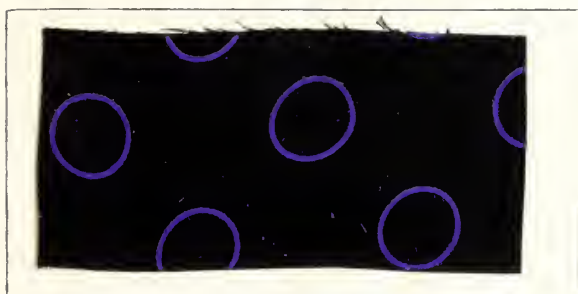
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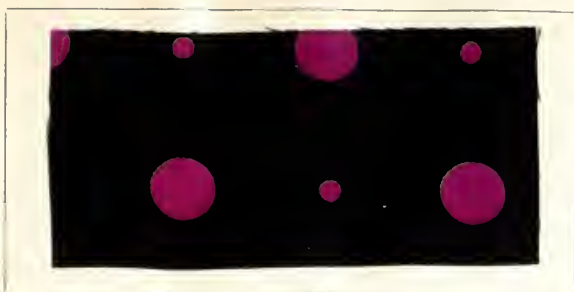
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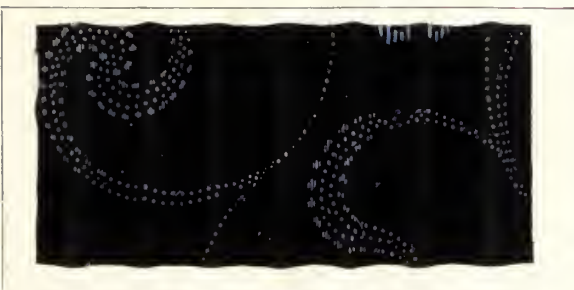
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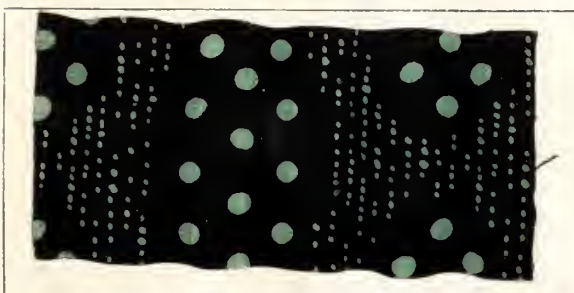
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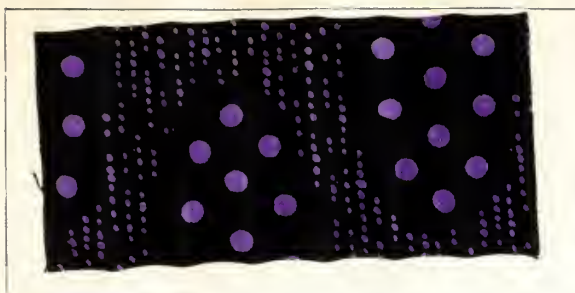
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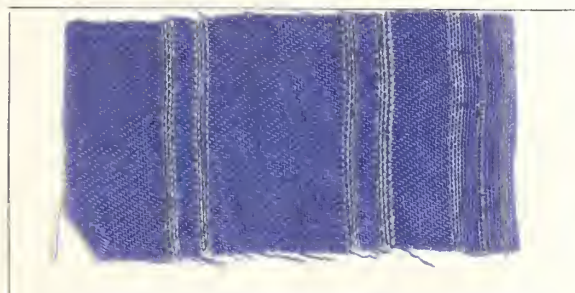
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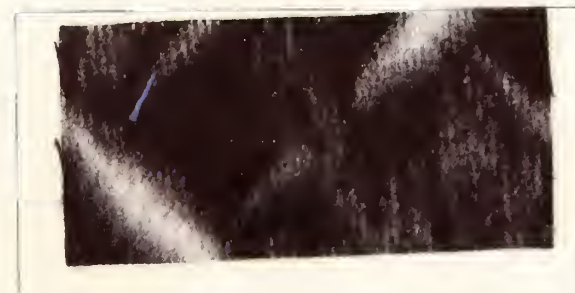
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No 18. DIAZO BLACK BHN.



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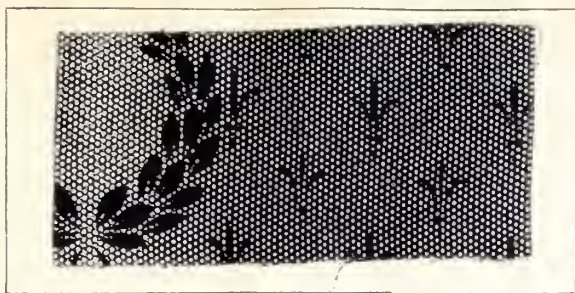
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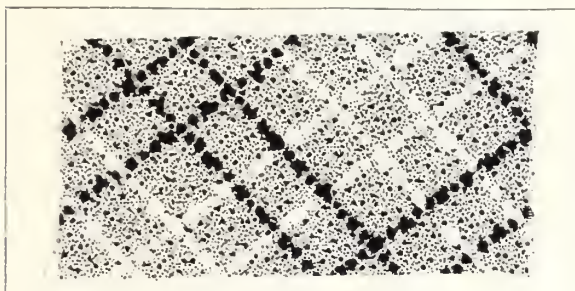
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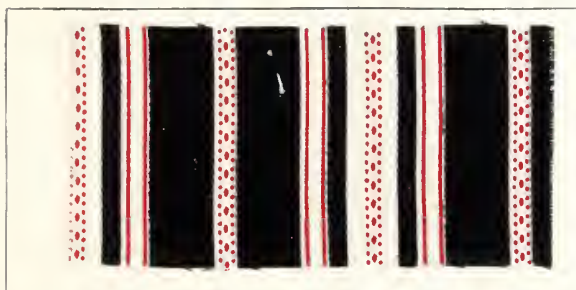
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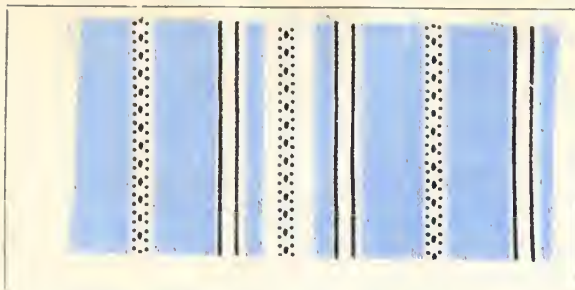
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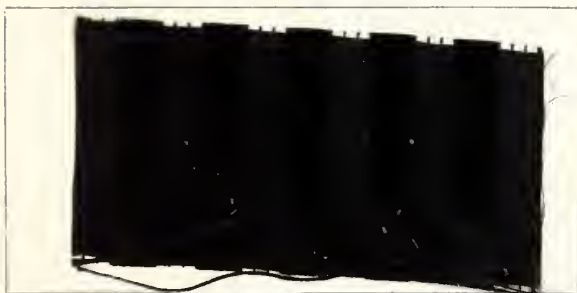
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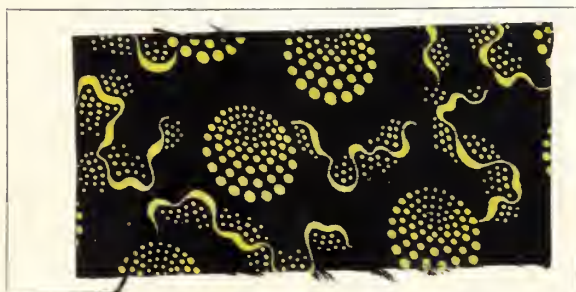
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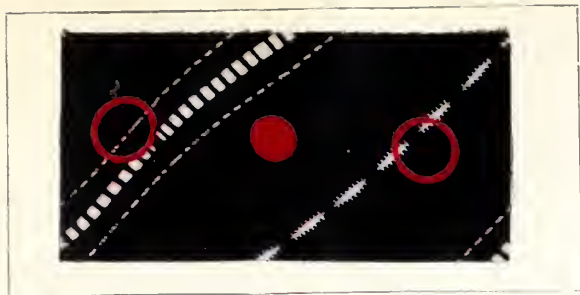
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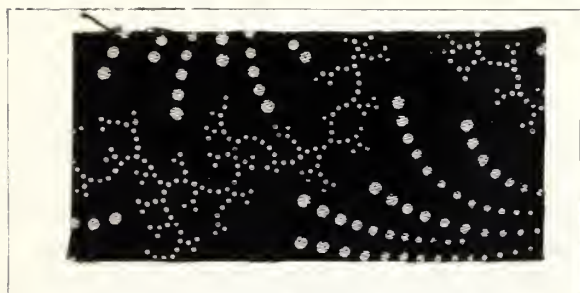
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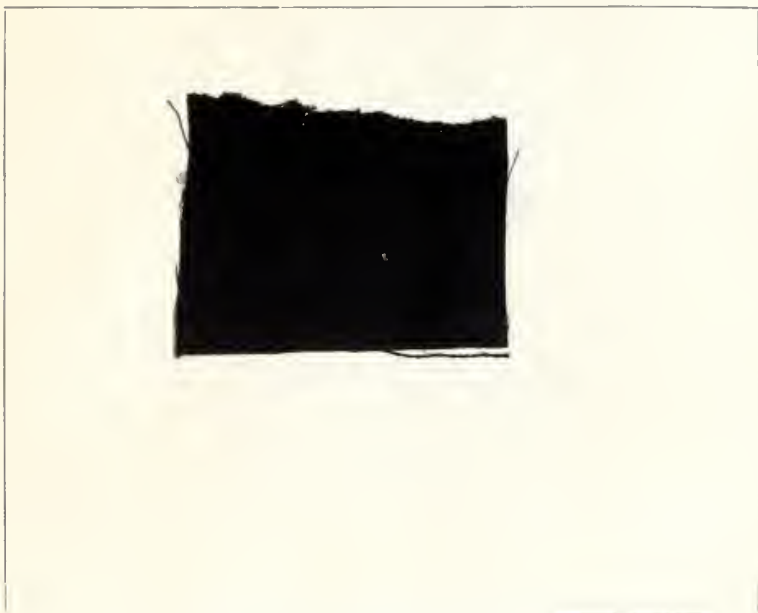
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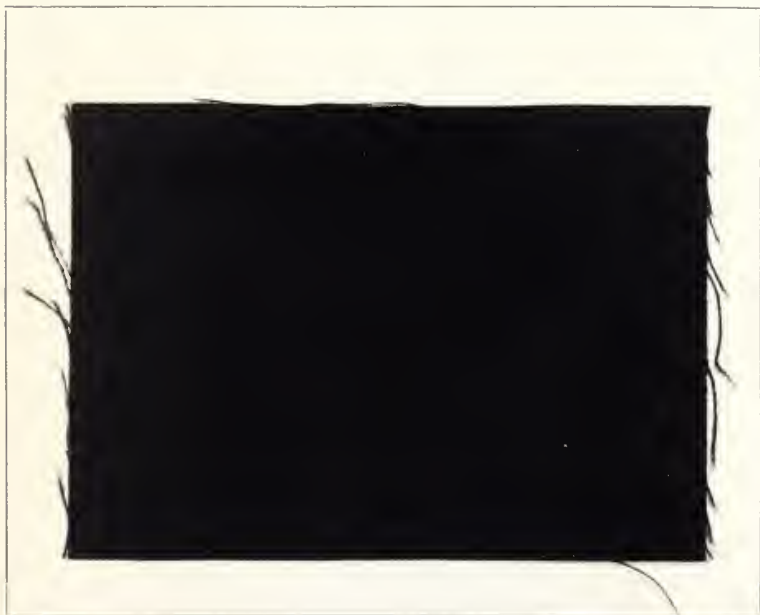
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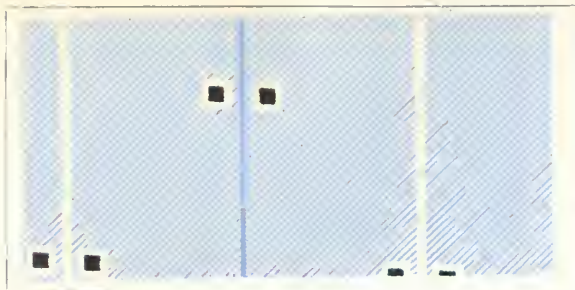
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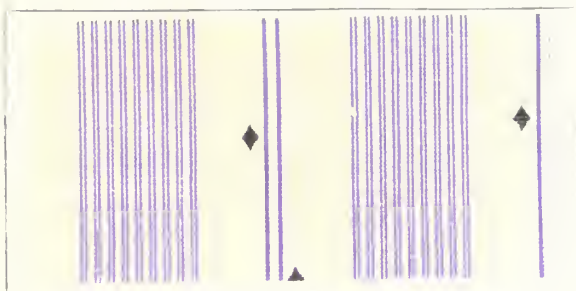
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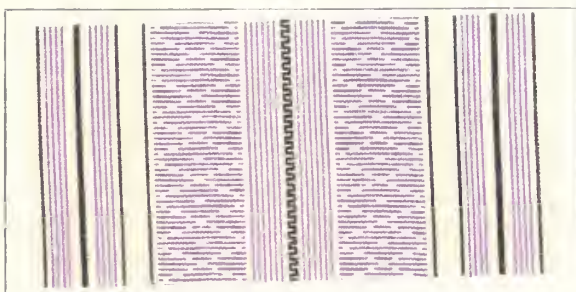
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